Analysis of Coffee Aroma Compounds by Headspace Solid-Phase Microextraction (SPME) GC-MS with the JMS Q1500GC Master-Quad GC-MS

INTRODUCTION

The composition of volatiles from freshly ground roasted coffee is complex, with hundreds of chemical compounds contributing to the aroma. Headspace solid-phase microextraction was used to sample volatiles from five different coffees for analysis by GC-MS. Chemometric analysis revealed specific differences between coffees from different origins and different preparations.

EXPERIMENTAL

Measurement
Four coffees purchased from a local coffee roaster were freshly ground for drip-filter preparation in the store. A fifth sample was purchased from a local grocery and ground to the same coarseness using an adjustable burr grinder. Approximately two grams of each ground coffee were placed in 20 mL headspace SPME vials for analysis. Five measurements were made for each sample except the decaffeinated Colombian coffee, for which only four replicates were measured. Table 1 shows the coffees analyzed.

An HTA HT2800T All-in-One autosampler was mounted on an Agilent 7890B GC used with a JEOL JMS-Q1500GC Master-Quad mass spectrometer. The autosampler was operated in SPME mode. Measurement conditions for the autosampler, GC and mass spectrometer are given in Table 2.

Data Analysis
Mass spectra measured by JEOL msPrimo software ware imported into AnalyzerProXD (SpectralWorks, UK) for chromatographic deconvolution, database search, and statistical analysis. The data processing parameters are given in Table 3. Column bleed peaks were omitted from the statistical analysis. Characteristic aroma descriptions are taken from the website listed in reference 1.

RESULTS

The total ion current chromatograms for individual replicates of each coffee are shown in Figure 1, with selected compounds labeled on the chromatograms. It is not trivial to determine small differences in the relative concentrations of specific compound by visual inspection alone.

Figure 2 shows the total ion current chromatogram for the third replicate measurement of the Colombian Supremo coffee headspace with compound assignments labeled for the major peaks.

Chromatographic deconvolution with AnalyzerPro XD is needed to identify trace peaks and peaks that are not completely separated. Figure 3 shows deconvolution of 1-Methylethenyl pyrazine, which overlaps with maltol (the larger peaks) in the Indian Malabar French Roast coffee headspace chromatogram.

Principal Component Analysis (PCA, Figure 4) shows distinct groupings for each coffee, with the Bali Blue Moon and the Columbian Supremo being the closest-matching clusters.

The data analysis showed distinctive differences between the coffees. For example, both of the Colombian coffees showed lower levels of pyridine than the other coffees (Figures 5 and 6.) The compound 5-methyl-2-furancarboxaldehyde with an aroma described as “sweet, caramellic, bready brown, coffee”[1] is very abundant in the Colombian Supremo and Bali coffees, but is at a relatively low abundance in the Indian Malabar French Roast.

The software permits easy comparisons for other compounds. For example, caffeine is at a relatively low level in the decaffeinated coffee, and some other compounds (e.g. pyrrole) are also at a reduced level in the decaffeinated coffee, perhaps because of the decaffeination process. The compound 1-methylethenyl pyrazine, which has an aroma described as “caramel, chocolate, nutty, roasted” and a “burnt coffee” flavor, is abundant in the Indian Malabar French Roast and Rwanda coffees, but at a relatively low level in the other coffees. The presence of that compound is not visually evident in the chromatogram because it is not chromatographically separated from maltol and other compounds, but it is revealed by chromatographic deconvolution.

CONCLUSION

Headspace SPME GC-MS analysis combined with statistical analysis provides a great deal of information about the chemical compounds contributing to coffee aroma. The JMS-Q1500GC GC-MS system equipped with the HTA HT2800T autosampler is an easy-to-use platform for data measurement, and data analysis with AnalyzerPro XD permits detailed comparisons between samples for specific compounds. It may be noted that some compounds could not be conclusively identified by database search alone. Conclusive identification of these unknowns may require soft ionization and high-resolution mass spectra that can be obtained with the JEOL AccuTOF GC-Alpha GC-HRTOFMS system [2].

REFERENCES

1. http://www.thegoodscentscompany.com/
2. https://www.jeolusa.com/RESOURCES/Analytical-Instruments/Documents-Downloads/comprehensive-analysis-unknown-component-analysis-of-coffee-samples-using-headspace-gc-ms

Sample	Origin	Note	Roast Level
1	Bali	"Blue Moon"	Medium Roast
2	Colombia	Decaffeinated	Medium Roast
3	India	Monsooned Malabar	French Roast
4	Rwanda	--	Medium Roast
5	Colombia	Supremo	Medium Roast

Table 1. Coffee Samples Analyzed

Autosampler		GC		MS	
Oven temperature	60°C	Column	Agilent CP-Sil 8 CB, 30 m, 0.32 mm diameter, 1 micron film thickness	Start	2 min
Conditioning time	10 min.	Injector	260 °C	End	55 min
Shaking Cycle	0.2 min on, 0.1 min off	Injection	Splitless	Mode	Scan
Extraction time	10 min.	Oven program	40°C(5 min), 4°C/min to 230°C, 50°C to 280(2 min)	Start m/z	40
Desorption time	5 min.	Flow rate	1.5 mL/min, constant flow	End m/z	400
SPME Fiber	100 micron PDMS, Supelco 57341-U	Gas	Helium	Cycles/s	2.11

Table 2. Measurement Conditions

Process as	Components		Scan window	4
Min. masses	3		S/N	5
Mass range	40-400		Smoothing	3
Reject masses	73, 147, 207, 281, 341, 325, 355		Fronting and Tailing	0%
Temporal resolution	Very Low		Width	0.02 min
Area threshold	80,000		Library Searching	NIST mainlib, replib

Table 3. Data Analysis Conditions

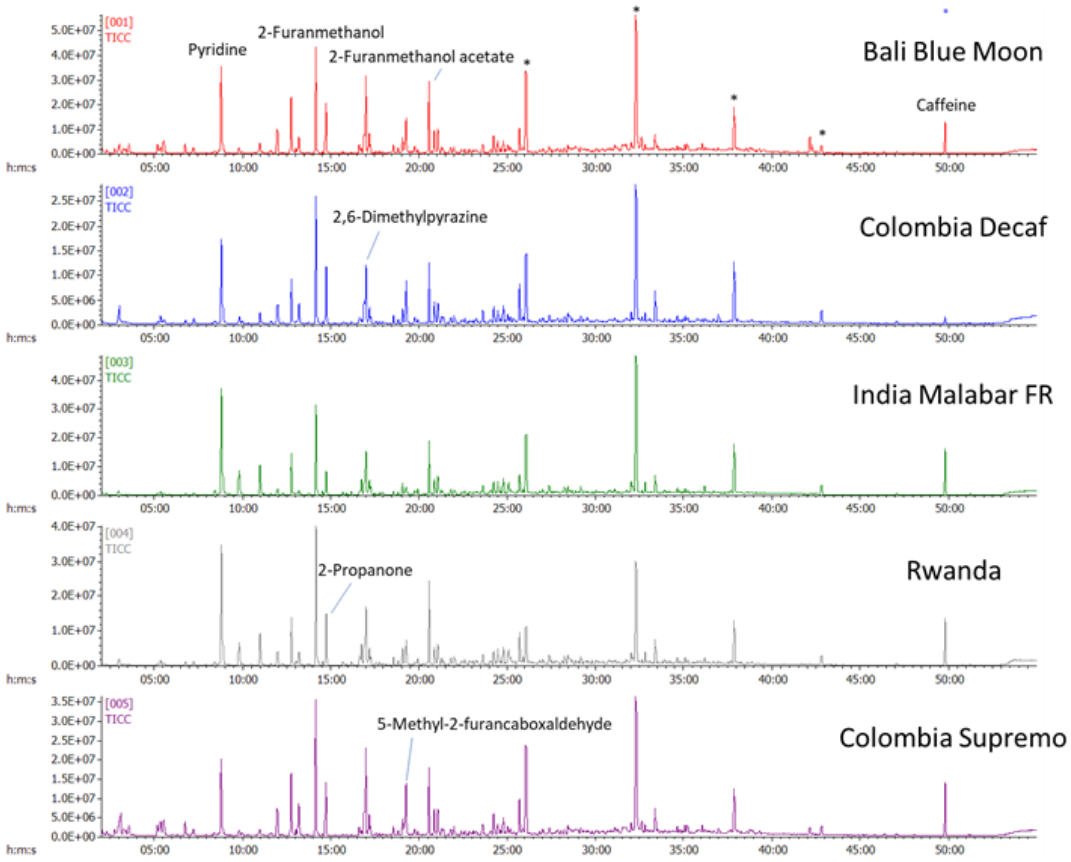

Figure 1. Total ion current chromatograms for the different coffees. Asterisks indicate silicone peaks.

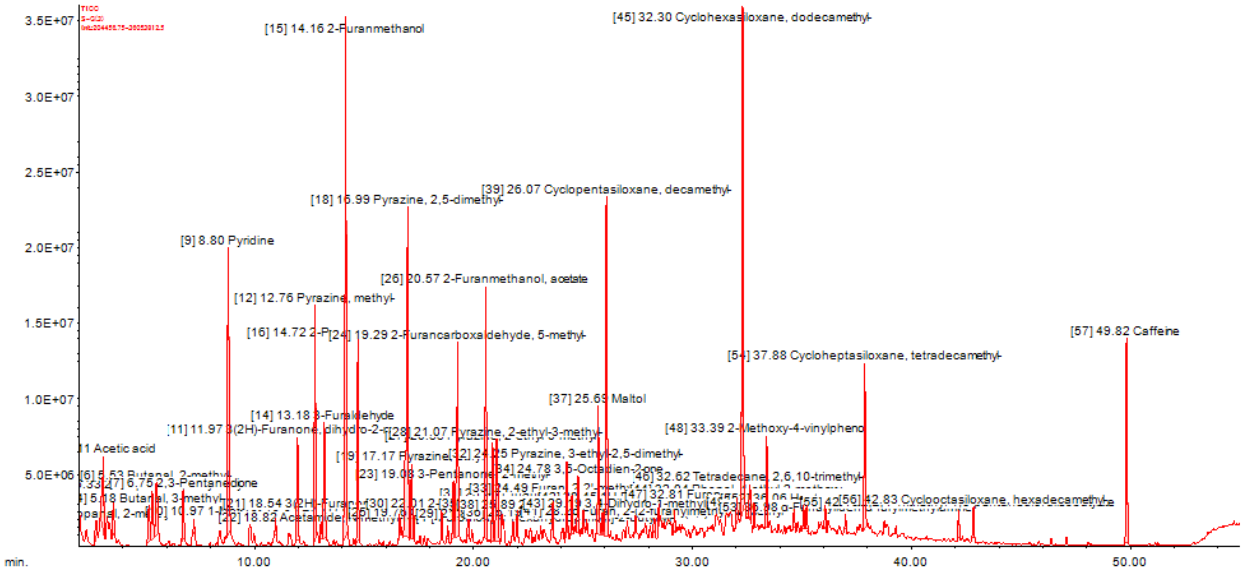

Figure 2. TICC for the Colombian Supremo coffee headspace with peak labels

Figure 3. Chromatographic deconvolution of 1-Methylethenyl pyrazine from maltol.

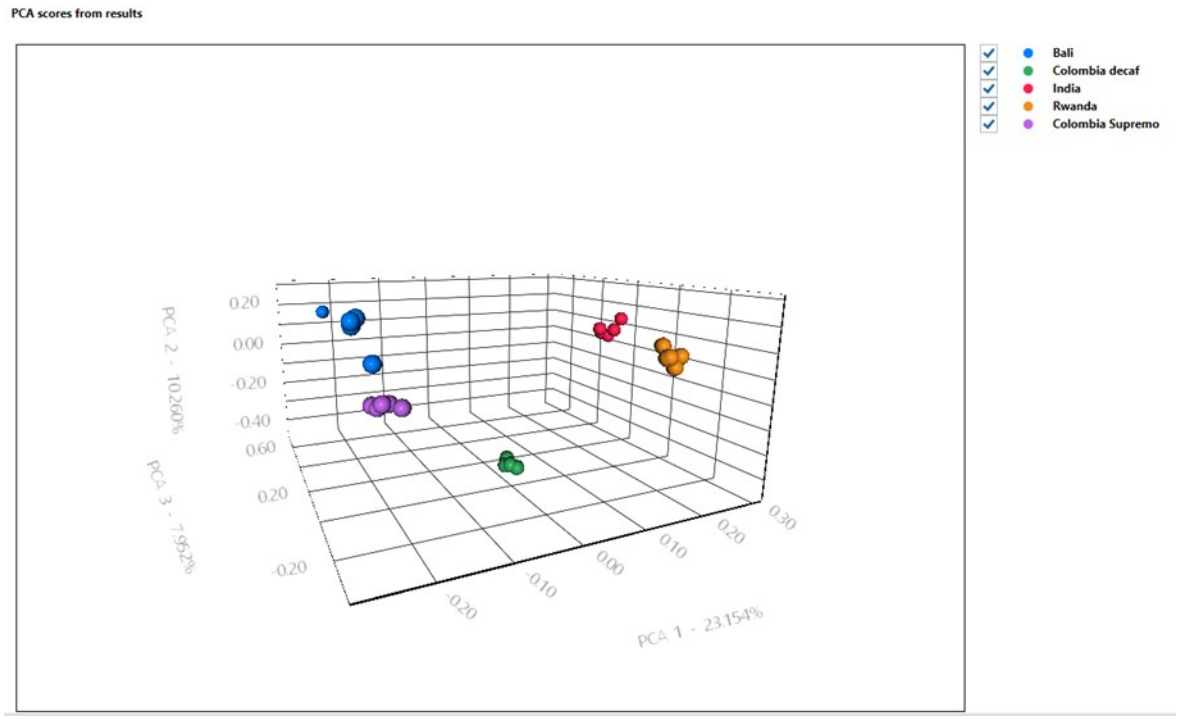

Figure 4. 3D-PCA Graph of the Coffees

Figure 5. PCA, Biplot, Box Plot and Mass Spectrum for Pyridine

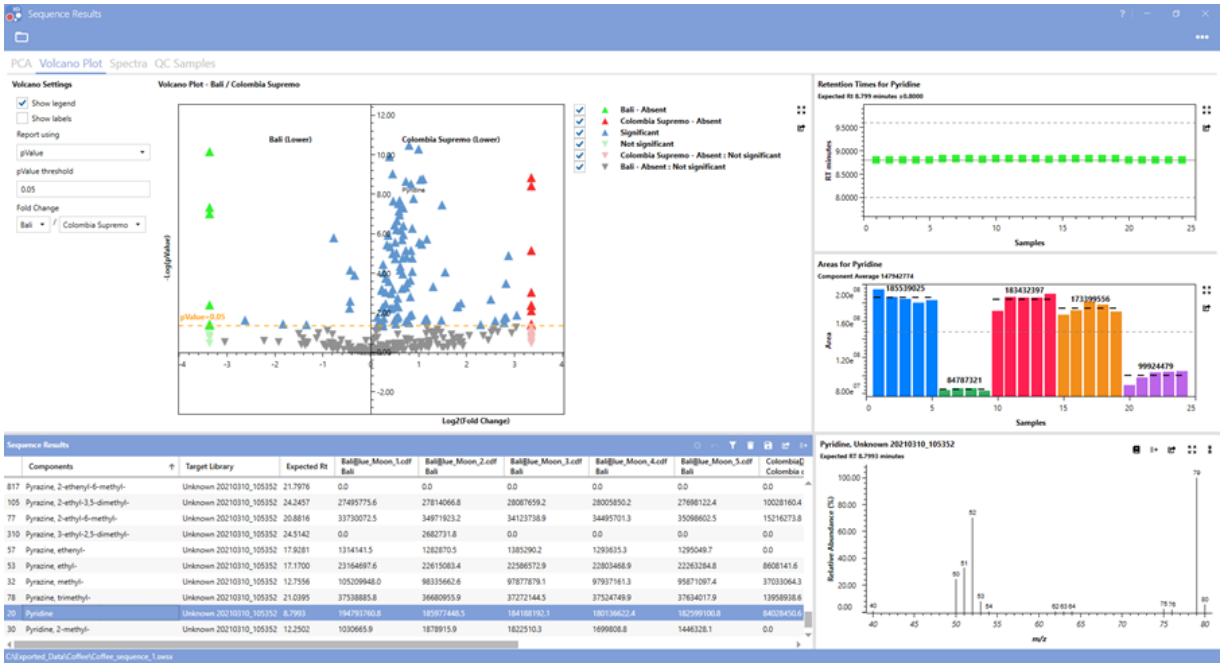

Figure 6. Volcano Plot comparing Bali and Colombian Supremo coffees and relative pyridine levels in all samples.

Figure 7. Relative abundance of 5-Methyl-2-furancarboxaldehyde in coffees

JMS-Q1500GC Master-Quad GC-MS System