



ACS FALL

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SUSTAINABILITY IN A CHANGING WORLD

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Sustainability in a
Changing World



New Discoveries in Coffee Aroma Research: The Aroma Impact of Trimethylamine

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Coffee Aroma – Enjoyed and Cherished Throughout the World



Coffee consumption statistics show that around **30-40%** of the **world's population** **consume coffee every day**.

In the USA, these figures are much higher and equate to **about 65%** of the total population.

[World Coffee Consumption Statistics – Coffee Rank \(coffee-rank.com\)](https://coffee-rank.com/)



Volatile Compounds Responsible for Coffee Aroma

Volatile compounds responsible for coffee aroma

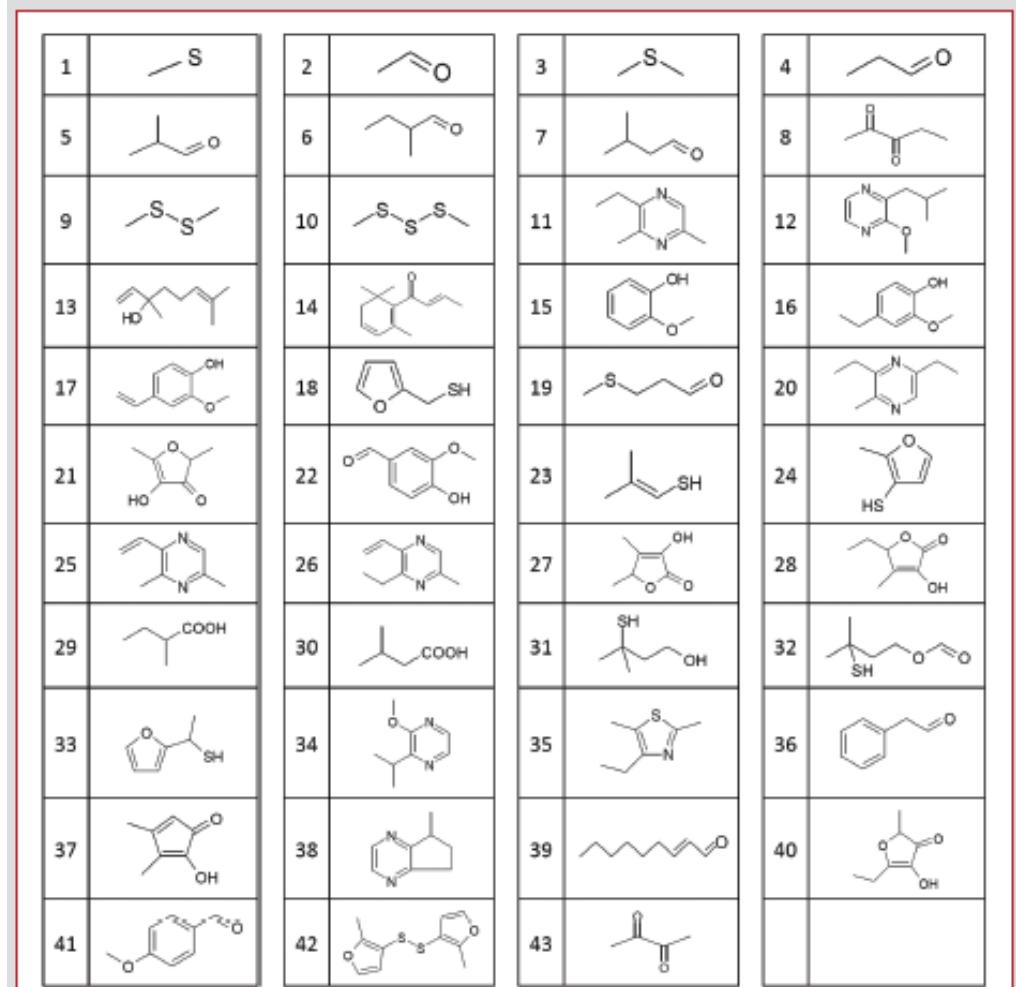
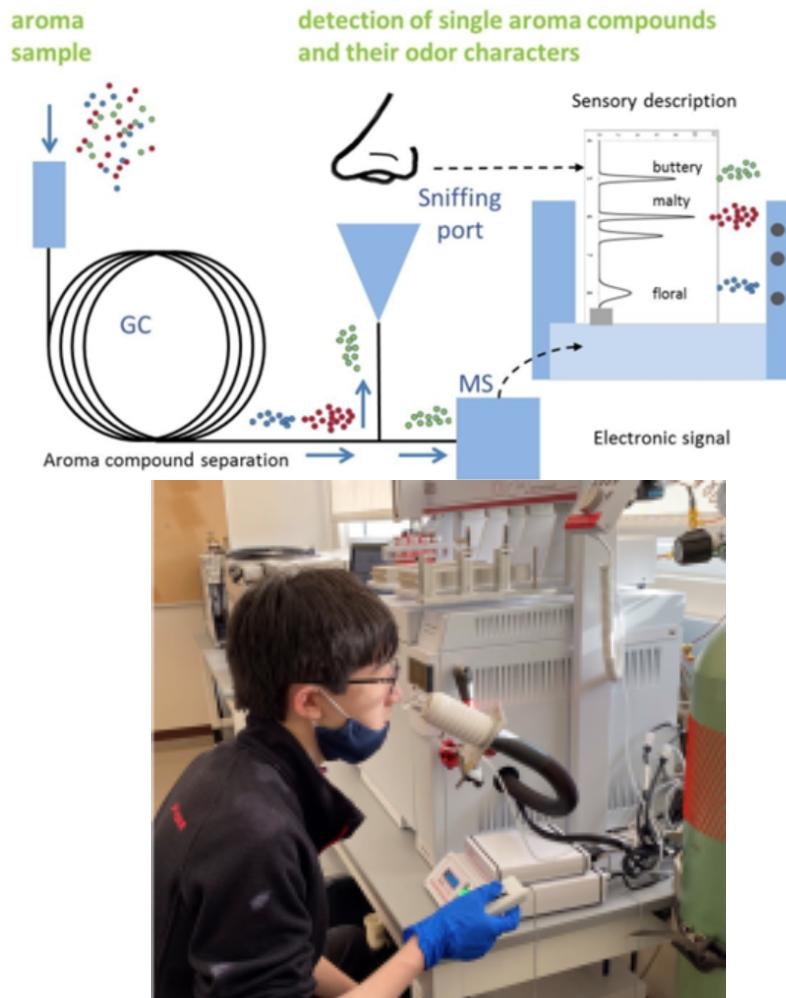


Figure 1 43 volatile compounds that contribute to the aroma of coffee

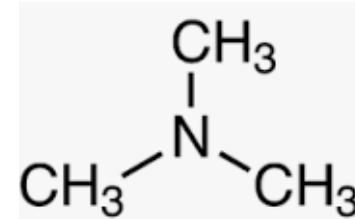
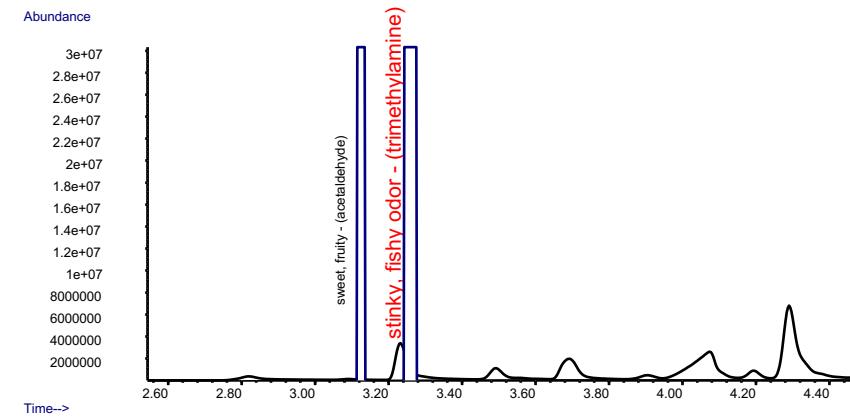
- Sulfur compounds
- Aldehydes
- Pyrazines
- Phenolics
- Furanones
- Acids



Trimethylamine : Detected by SPME-GC-MS-O on French R&G Coffee



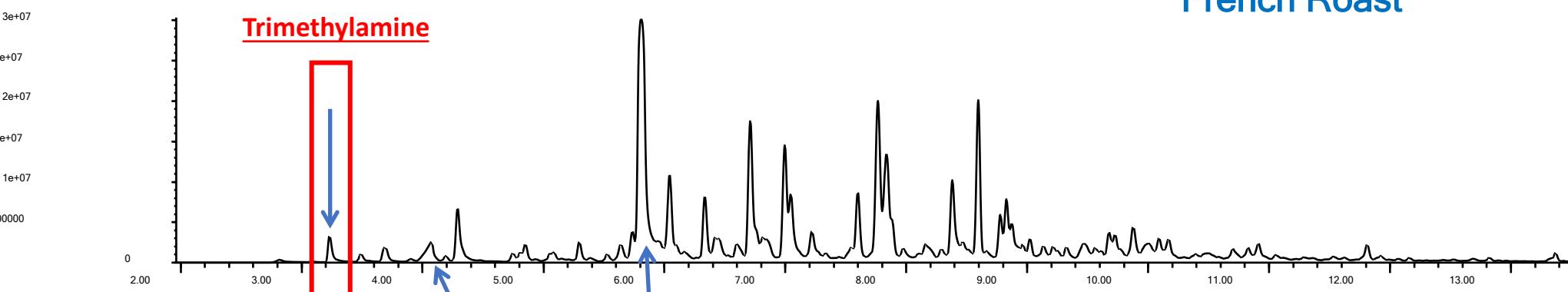
SPME-GC-MS-Olfactometry: TMA is very perceivable in French Roast



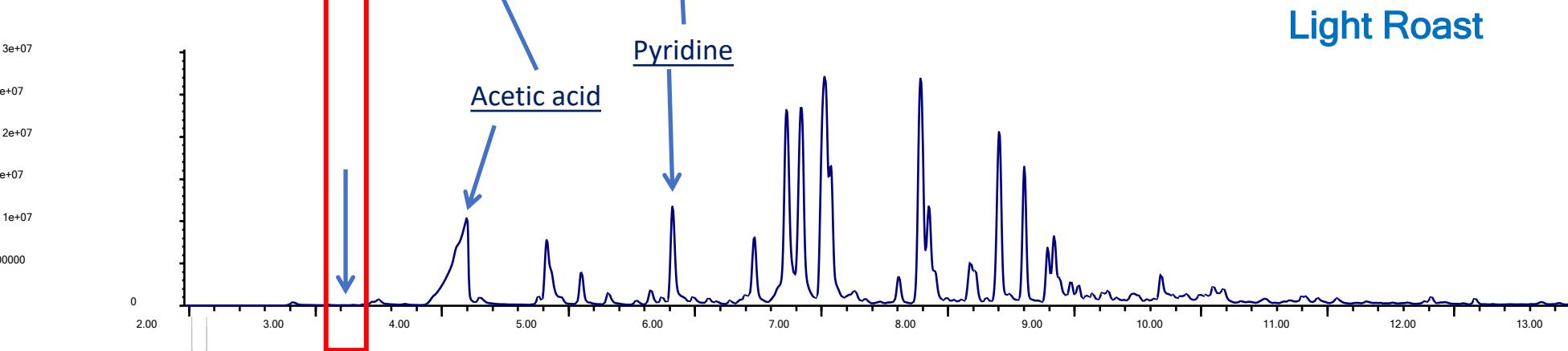
SPME-GC-MS of Roast and Ground Coffee Samples

Observations: Trimethylamine (TMA) is higher in darker roasted coffees

Abundance



Time-->
Abundance

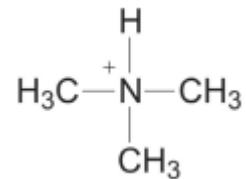


Time-->



Characteristics of TMA : Make Analysis and Detection Challenging

- Highly water soluble : not detected in SPME above brew; difficult to extract with organic solvents
- pKa 9.57: protonated in coffee beverage (lowers the volatility and inhibits analysis by headspace)
- Strong fishy odor: low odor detection threshold in air (0.21 ppb)*



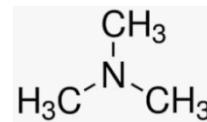
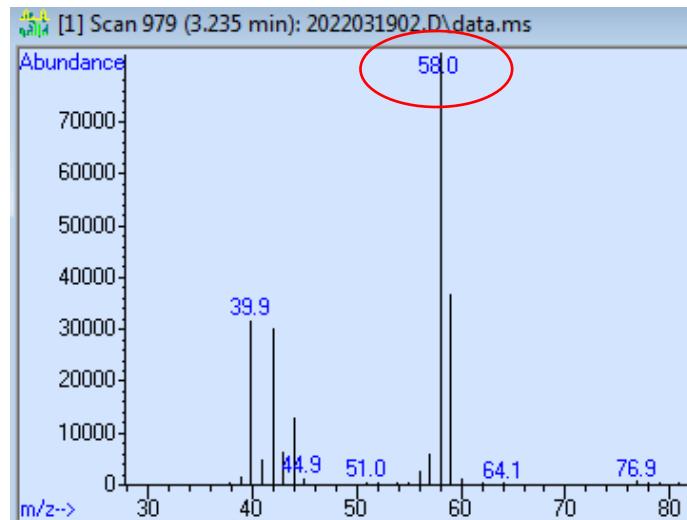
- Approach:
 - (1) Use stable isotope as internal standard (trimethylamine-d₉)
 - (2) Add buffer to raise pH above 9 to enable analysis by SPME-GC-MS

*Leonardos et. al. (1969) Odor Threshold determination of 53 odorant chemicals



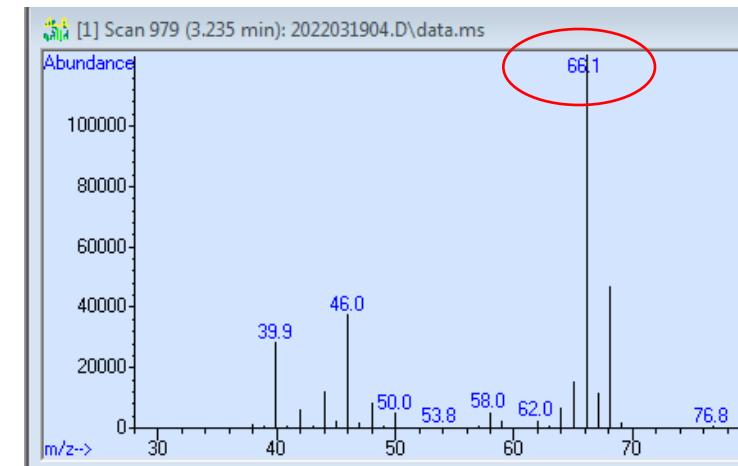
Mass Spectra for Trimethylamine and Trimethylamine-d₉

TMA mass spectrum



59.11 g/mol

d⁹-TMA mass spectrum



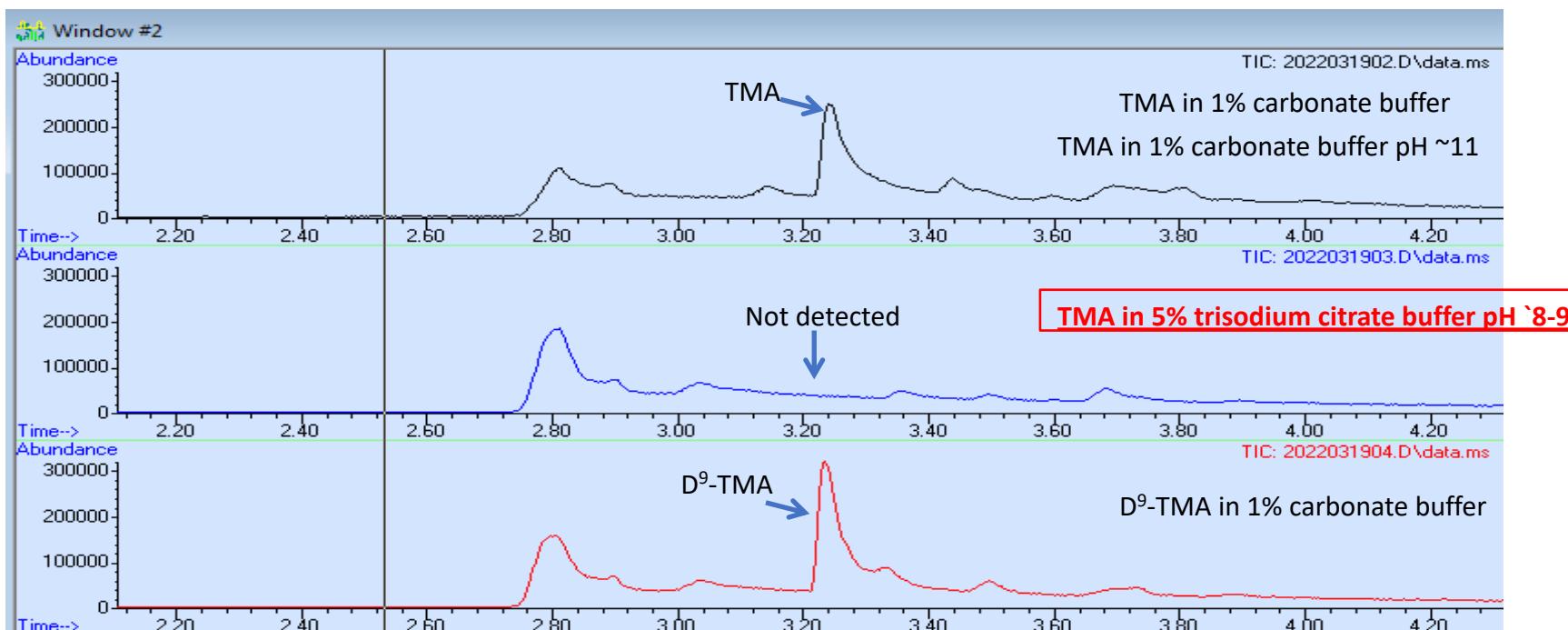
68.11 g/mol

Peak areas for m/z = 58 and m/z = 66 were determined and the ratio of 58/66 was used for development of calibration curve



Carbonate Buffer Enables Detection of TMA by SPME-GC-MS

- Stable Isototope as internal standard: Trimethyl-d₉-amine HCl from CDN Isotopes
- Buffer: Trisodium citrate vs sodium carbonate
- SPME-GC-MS: TMA/d₉-TMA calibration curve

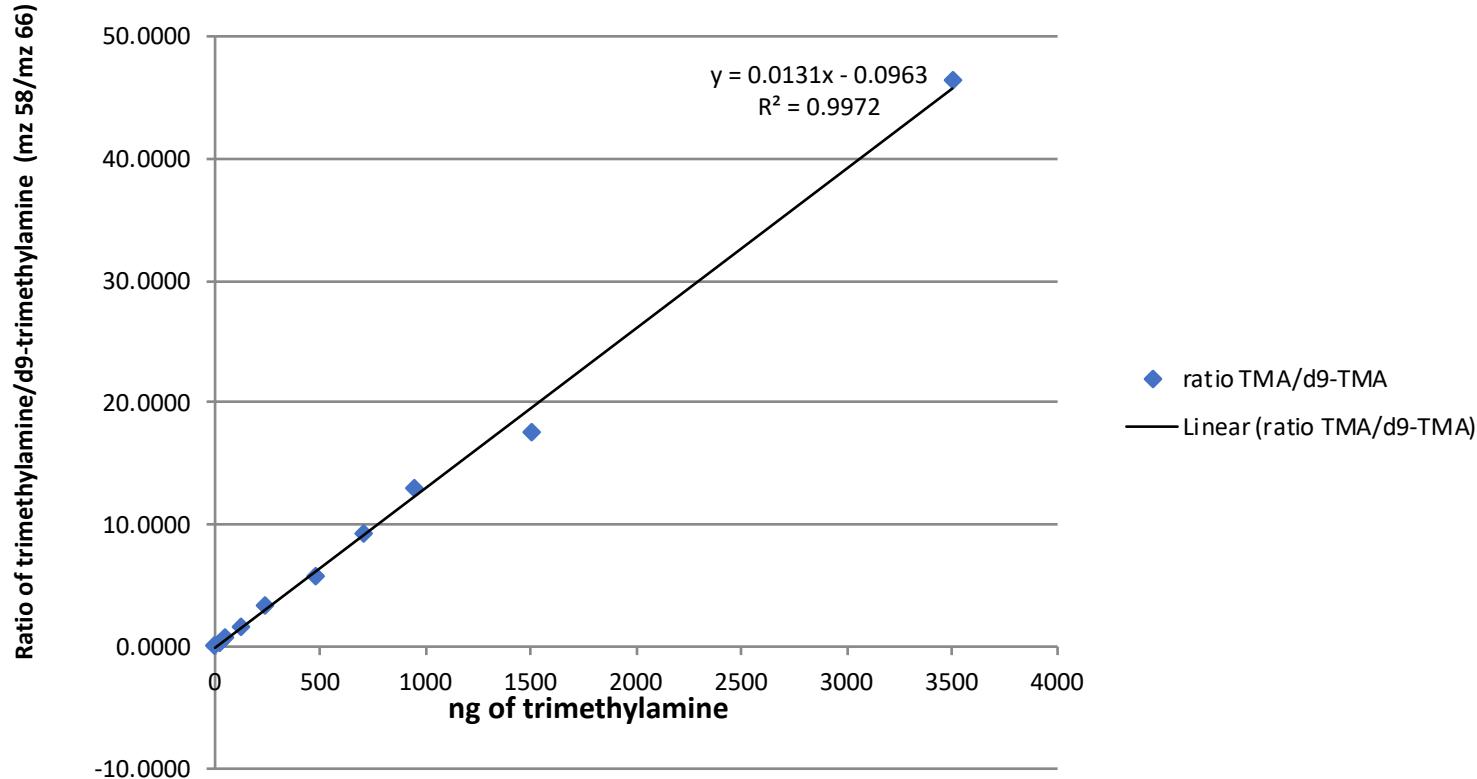


Results:

- pKa of trimethylamine is around 9.8 and in aqueous system, the pH needs to be above that for it to be volatile and detected by headspace technique.
- Trisodium citrate buffer is not basic enough to work
- Sodium carbonate buffer is more basic and then we can see the TMA
- Using d₉-TMA as an internal standard is the best approach because it behaves exactly as the TMA and will result in good quantitation results.



TMA Method Development: Standard Curve



- 10-point calibration curve
- 0-3500 ng trimethylamine
- $R^2 = 0.997$



TMA Method Development: Coffee Analysis

Procedure:

- Weigh 0.05 to 0.10 g of ground coffee into 22-mL SPME headspace vial
- Add 3 mL of 1% sodium carbonate solution
- Add 50 ul of 1ppm solution of trimethylamine (d9) in deionized water
- SPME: MPS Autosampler
 - 10 min equilibration at 50°C with agitation
 - 10 min extraction with 2-cm 3-phase (DVB/Carb/PDMS) SPME fiber at 50°C with agitation.
 - Desorb into GC-MS (DB-5MS)
- GC conditions:
 - Initial temp 50°C (hold 1 min); ramp at 15°C/min to 250 (hold 5 min).
- MS Conditions:
 - Full Scan (m/z : 35-350); no solvent delay



Coffee Samples for Trimethylamine Analysis

Light Roast



Med Roast



Dark Roast



TMA Levels in Various Coffee Samples : Higher in Darker Roasted Products

<u>Brand</u>	<u>Coffee sample</u>	<u>ppm (ug/g) TMA in sample</u>	<u>Average (ppm)</u>
Starbucks	Veranda blend	25.8	23.8
	Veranda blend	21.7	
	Pike Place	37.6	38.4
	Pike Place	39.1	
	French Roast	60.6	57.1
	French Roast	57.6	
	French Roast	54.7	
	French Roast	55.5	57.1
	Starbucks Espresso Roast	56.0	
	Starbucks Espresso Roast	58.2	
Dunkin Donuts	Dunkin Donuts Original	18.8	19.6
	Dunkin Donuts Original	20.4	
	Dunkin Donuts Midnight Roast	47.9	49.7
	Dunkin Donuts Midnight Roast	51.6	
McDonalds	McCafe	20.6	20.2
	McCafe	19.9	
Caribou	Caribou Blend Med Roast	40.4	39.8
	Caribou Blend Med Roast	39.1	
	Caribou Daybreak	25.4	23.7
	Caribou Daybreak	21.9	

Spike & Recovery on Caribou

Daybreak

- 5 sample spikes (1.538ug TMA) = ~1.5x
- 99.4% recovery
- 4.64% relative standard deviation
- 23.7ppm used as existing level coffee



Summary

- Identified trimethylamine (TMA) as an important aroma contributor to ground coffee of dark roasted coffee samples
- Developed a reproducible and simple method for TMA quantitation in coffee samples
- To our knowledge, this is the first set of data on TMA levels in coffee



Acknowledgements

Department of Chemistry, Eastern Kentucky University

