New Discovery in Coffee Aroma Research:

The Aroma Impact of Trimethylamine (TMA)

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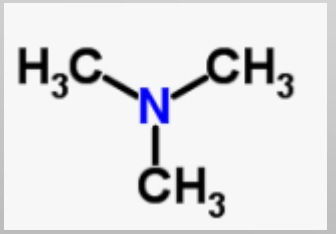


Coffee Aroma

Enjoyed and Cherished Throughout the World

Coffee consumption statistics show that around ***30-40%*** of the ***world's population consume coffee every day***. [1]

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

Summary of Literature Search on Coffee Aroma

Volatile Compounds Contributing to Coffee Aroma

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

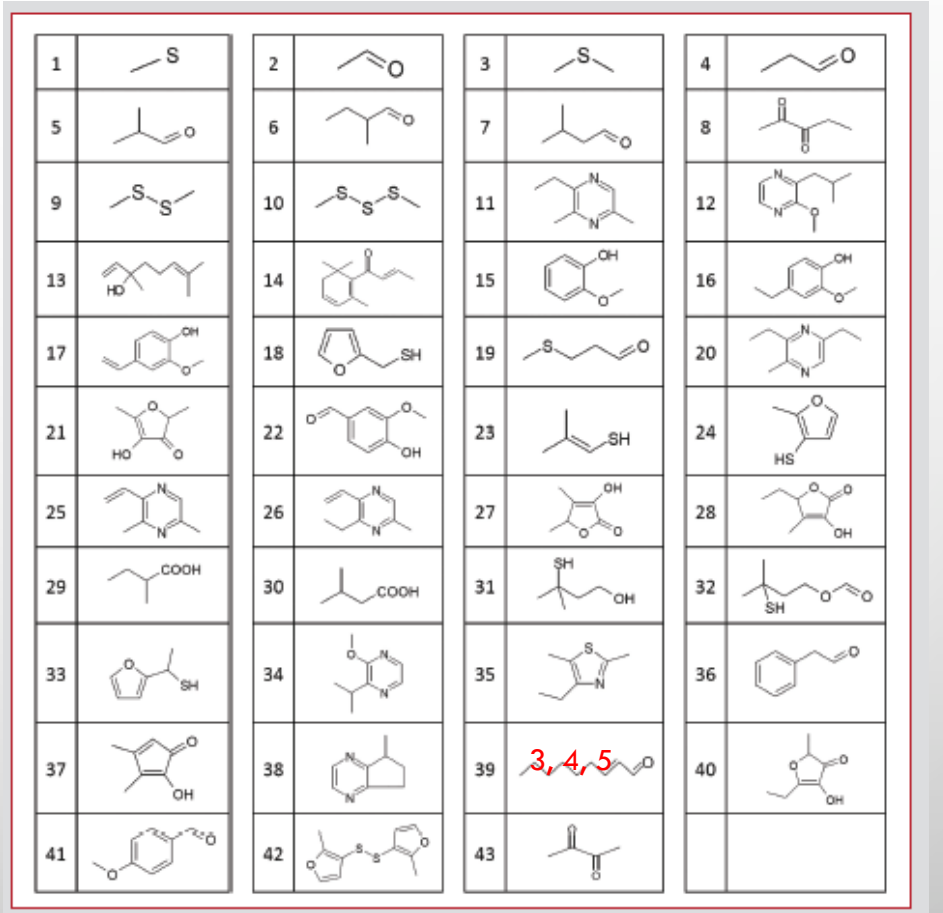


Figure 1 43 volatile compounds that contribute to the aroma of coffee

Observation and Hypothesis

Observation: Mixing all the known volatile compounds together has not resulted in an identical coffee aroma profile[2,4].

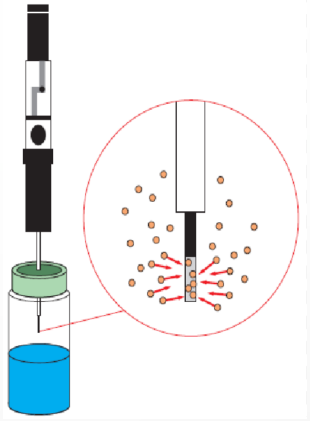
Hypothesis: There are additional compound(s) which contribute significantly to coffee aroma, which have not been discovered.

Significance and Impact of this Research:

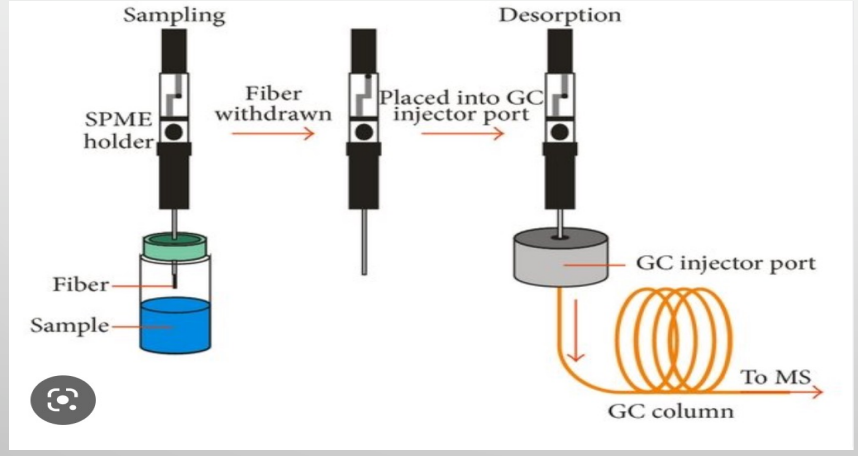
- Leads to development of a more authentic coffee aroma formulation
- Valuable tool for companies that develop flavors and fragrances
- The coffee aroma flavor and fragrance are used in daily products:
  - foods,
  - beverages,
  - candles , and etc.

Techniques

- **Solid phase microextraction (SPME)**

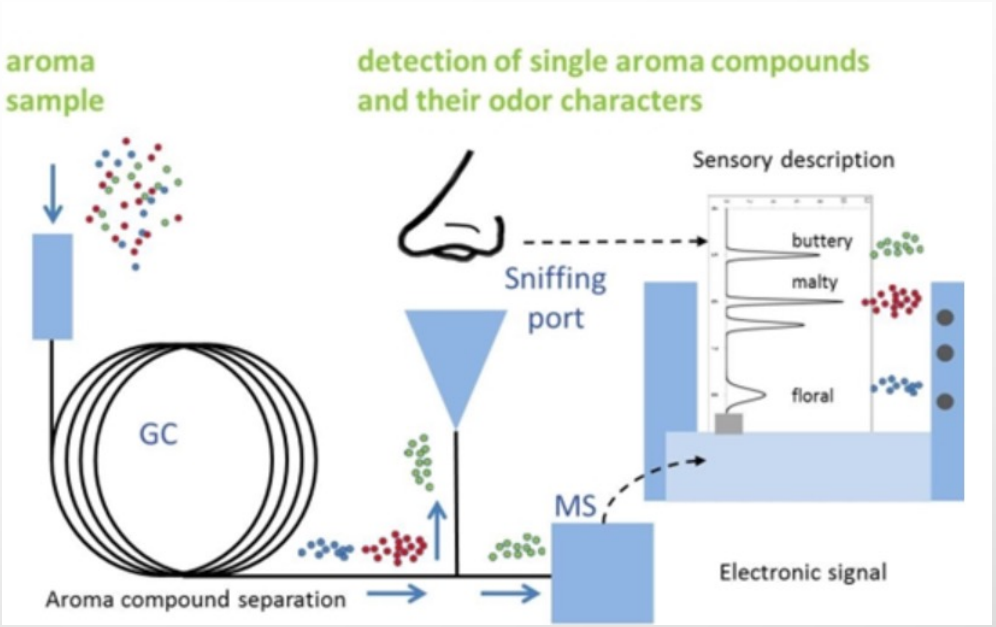


- **Gas Chromatography Mass Spectrometry (GC-MS)**



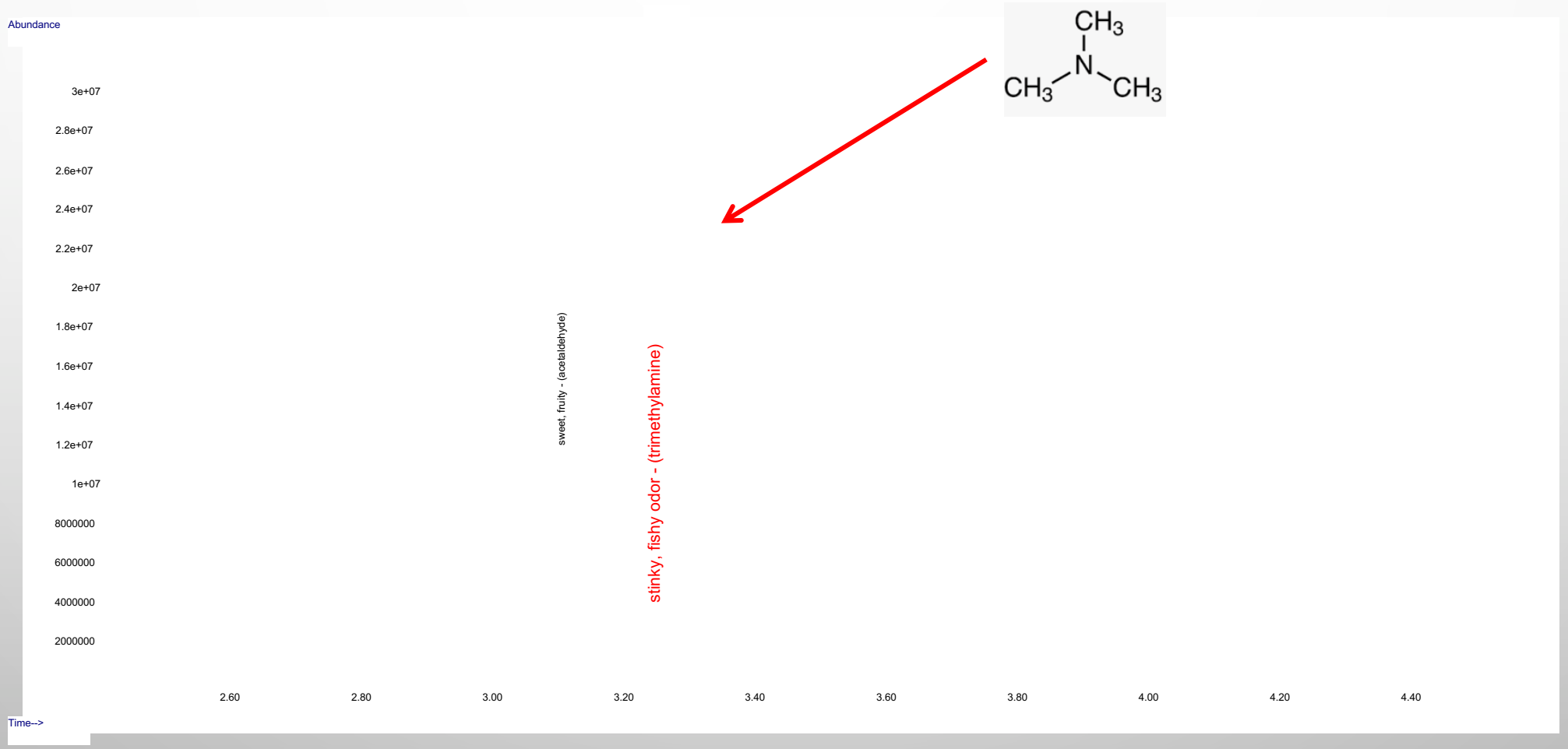
Techniques

- **Gas Chromatography – Olfactometry (GC-O)**



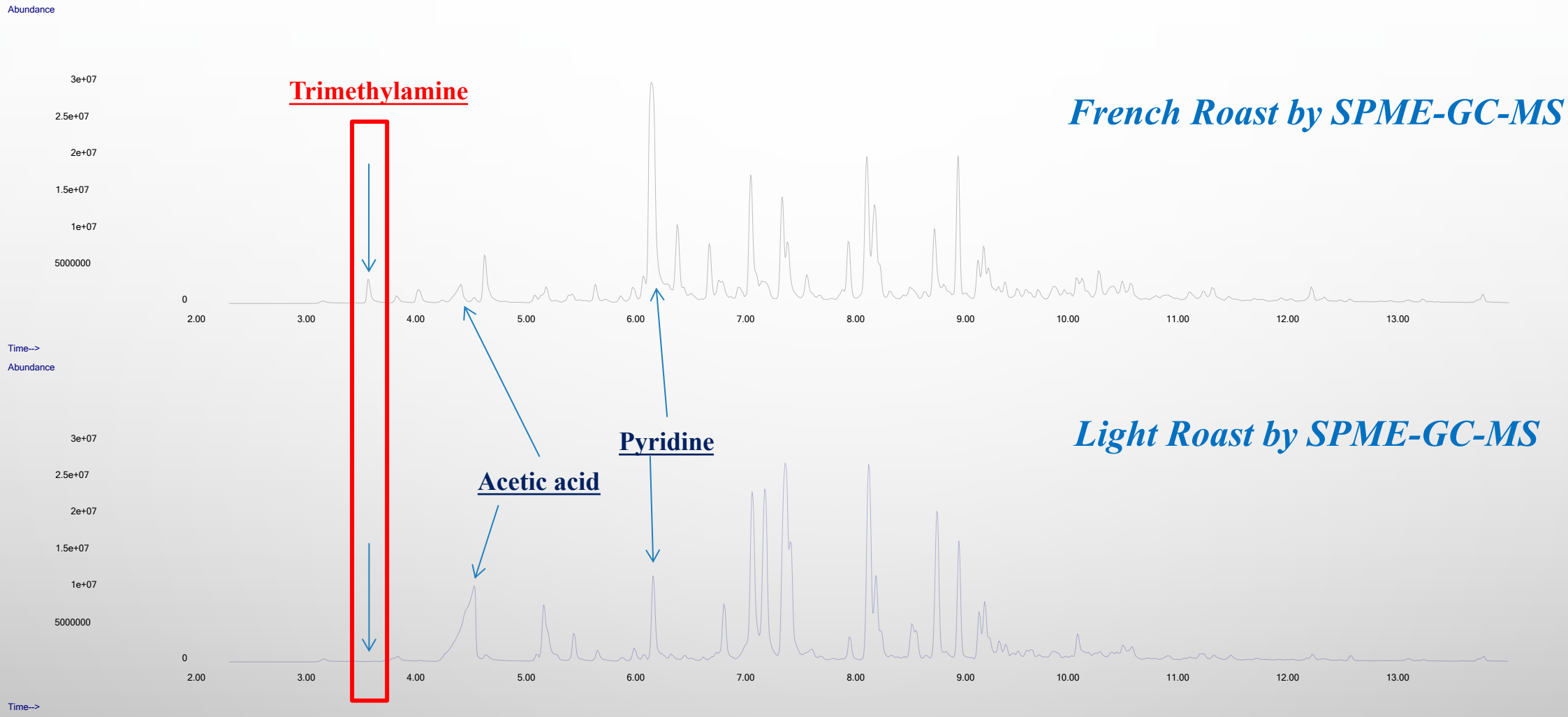
SPME-GCO Results

- Trimethylamine (TMA) detected as a very perceivable strong aroma contributor in French Roasted Coffee

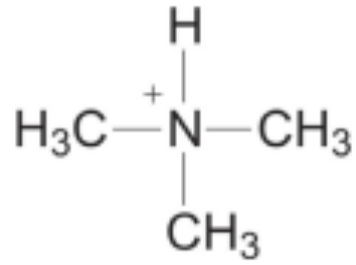


SPME-GC-MS Results

- TMA: More Prominent in Dark Roasted Coffees



Challenging Characteristics of TMA



- 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)[6]

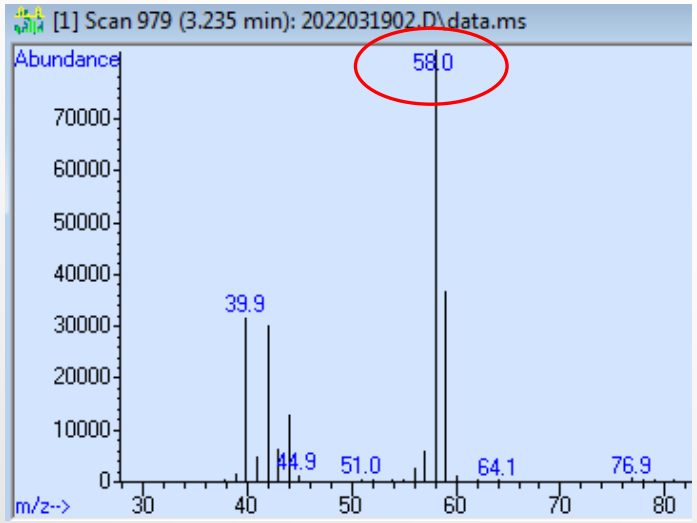
Most flavor molecules are hydrophobic and are easily extracted with organic solvents, but TMA is different.

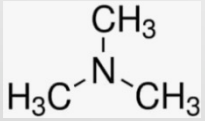
Our Approach:

(1) Use stable isotope as internal standard (trimethylamine-d_9)
(2) Add buffer to raise pH above 9 to enable analysis by SPME-GC-MS

Mass Spectrum Differences: Trimethylamine versus d^9-Trimethylamine

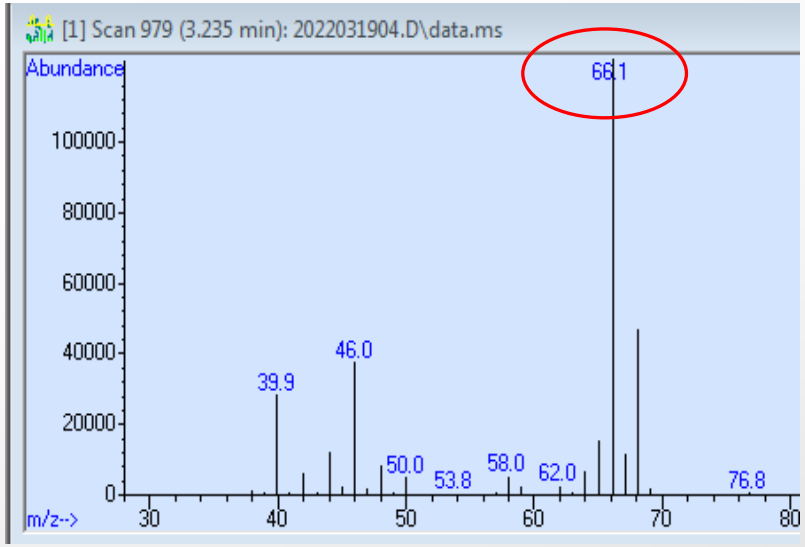
TMA mass spectrum





59.11 g/mol

d^9-TMA mass spectrum



$(CD_3)_3N$

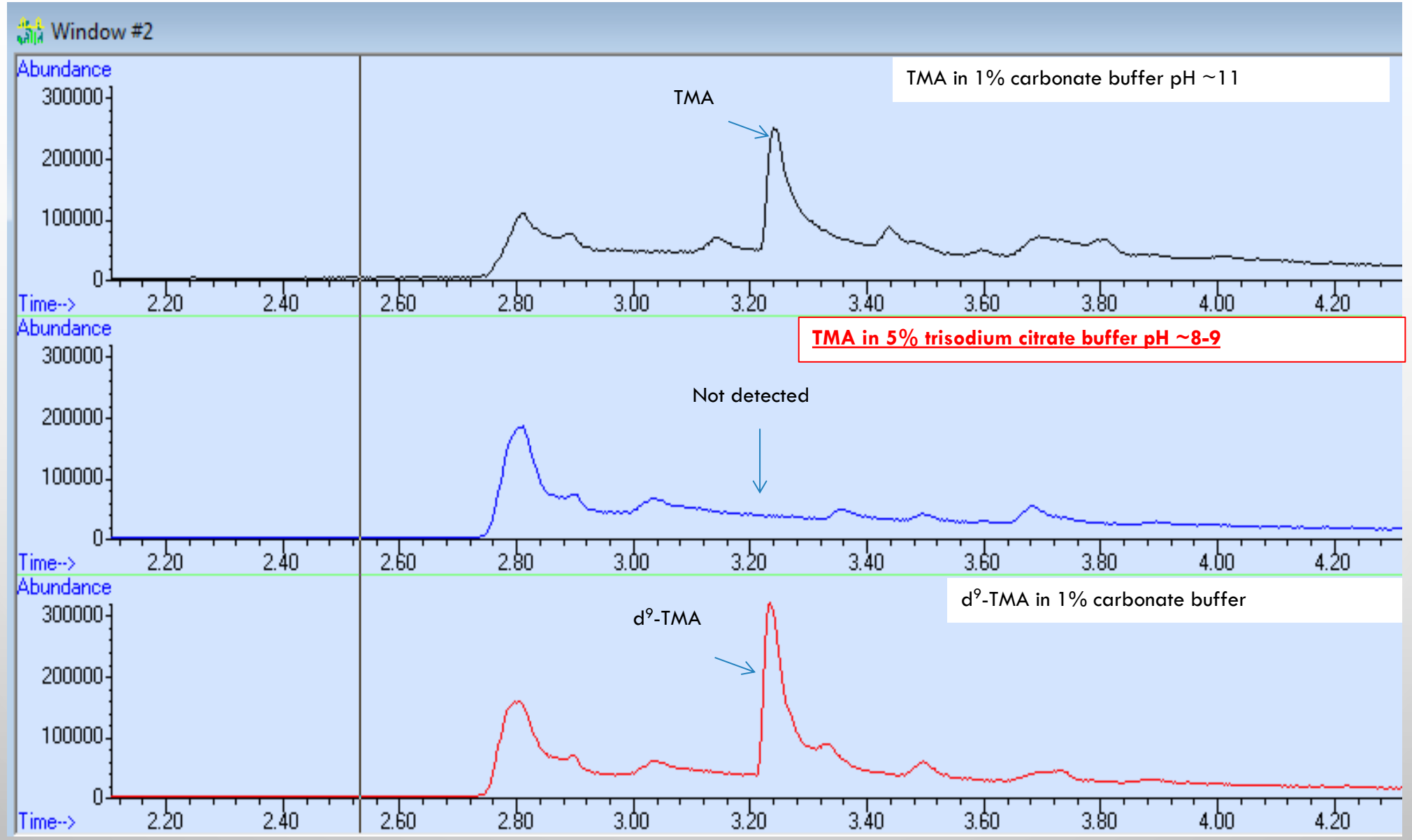
68.11 g/mol

- Peak area amounts for extracted ions m/z = 58 and m/z = 66 were determined
- Ratio of 58/66 was used for development of calibration curve

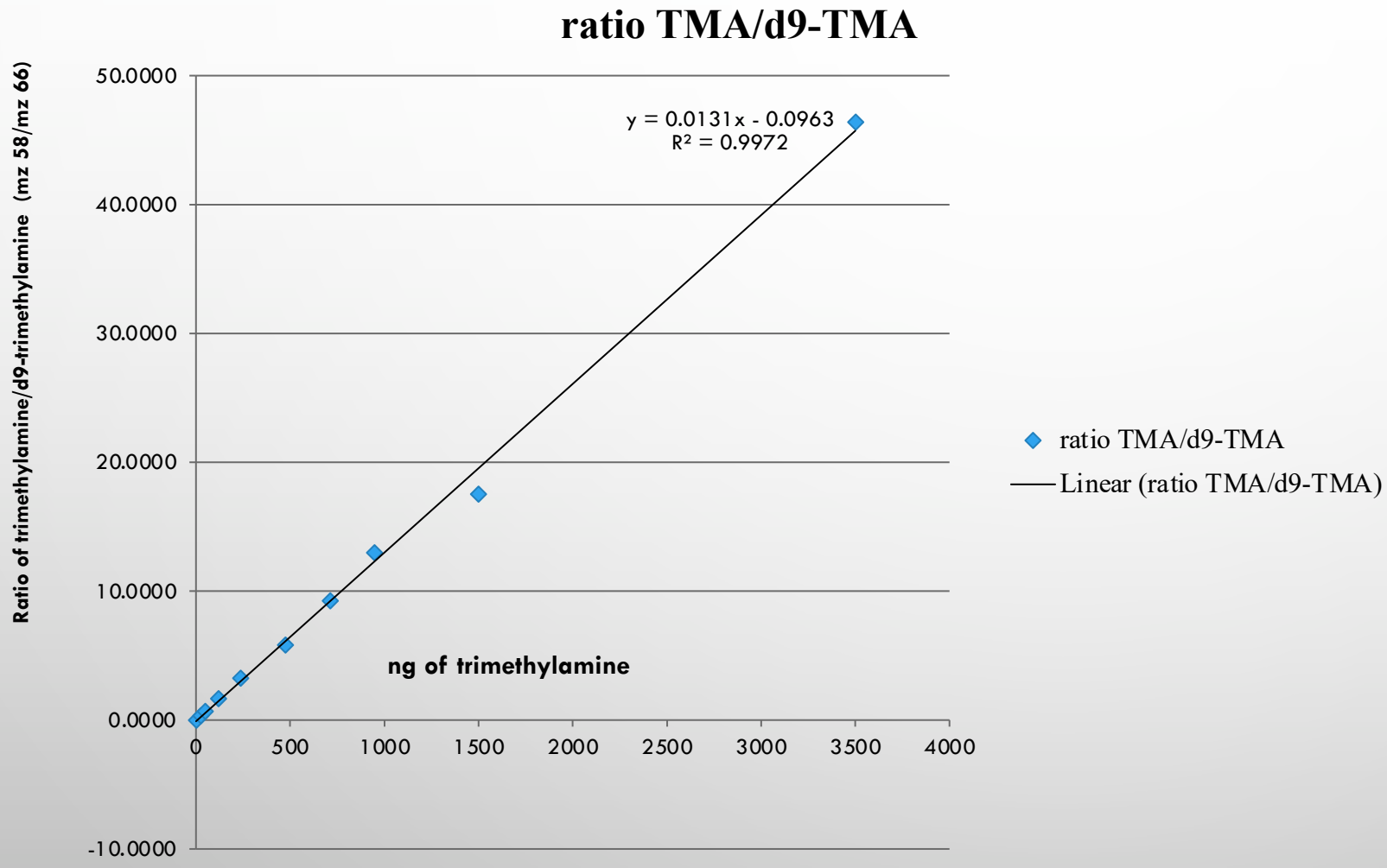
TMA Detection

- pKa of trimethylamine is around 9.57 and in aqueous systems, 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 thus enables detection of 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.

Carbonate Buffer Enabled Detection to TMA (SPME-GC-MS)



Development of TMA Standard Curve: Using SPME-GC-MS



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

Procedure for Measuring TMA in Coffee Samples

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

Trimethylamine Levels in the Various Coffee Samples (Highest in Dark Roast)

Brand	Coffee sample	ppm (ug/g) TMA in sample	Average (ppm)
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	
	Starbucks Espresso Roast	56.0	57.1
	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	

TMA Range: 19.6 – 57.1 ppm

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	French Roast	54.7	
	French Roast	55.5	
	Starbucks Espresso Roast	56.0	57.1
	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	
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	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

Conclusions

NEW DISCOVERIES!

- Identified trimethylamine as an important aroma contributor to ground coffee of dark roasted coffee samples.

- Developed a new reproducible and simple method for TMA quantitation in coffee samples

Summary

- This knowledge has the potential to serve as a valuable tool for creation of more “authentic coffee aromas” by flavor and fragrance companies, which will in turn be applied to various beverage products or used in scented fragrance products (candles, air fresheners) to enhance quality of life.

- To our knowledge, this is the first set of data on TMA levels in coffee. Therefore, we are currently working on a manuscript for publication.

Acknowledgements

- Ms. Deborah Haggard, my high school chemistry teacher and mentor

- EKU and Dr. Zyzak for allowing the usage of her research equipment and lab space

References

[1]World Coffee Consumption Statistics – Coffee Rank (coffee-rank.com)

[2]TAssessmet of the contribution of new aroma compounds found in coffee to the aroma of coffee brews (2004) Poisson, L., Kerler, J., and Liardon, R. *State-of-the-Art in Flavour Chemistry and Biology, Proceedngs of the Wartburg Symposium on Flavour Chemistry and Biology, 7th, Eisenach, Germany, Apr. 21-23, 2004 pp. 495-498.*

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[4]The kinetics of coffee aroma extraction (2014) Mestdagh, F., Davidek, T., Chaumonteuil, M., Folmer, B., Blank, I. *Food Research International* p. 271-274

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[6]Leonardos et. al. (1969) Odor Threshold determination of 53 odorant chemicals