Flavor analysis and research at the University of Minnesota

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Agenda

- Introduction
- Presentation of Research
- Questions

Flavor Laboratory

Professor Dr. Gary Reineccius

- 2 Research associates
- 1 Post-doctoral
- 9 graduate students
  - 4 M.S.
  - 5 Ph.D.
- 2 interns
- 2 technicians

Flavor laboratory (cont.)

- Diversity
  - People
  - Projects
- Strong ties to Industry
  - Short term issues: Off-flavor issues
  - Long term research (proprietary)

Research

- Diverse
  - Stability of flavor emulsions
  - Flavor performance as affected by process
    - Raw ingredients
    - Physical parameters
      - Cooking temperature
      - Storage (temperature, time)
  - Flavor release

Flavor analysis 101

FLAVOR EXTRACTION

- multitude of possible protocols, all biased
- single analysis rarely enough depending of goals
- probably the most under estimated portion

CHEMICAL ANALYSIS

- injection
- separation
- detection

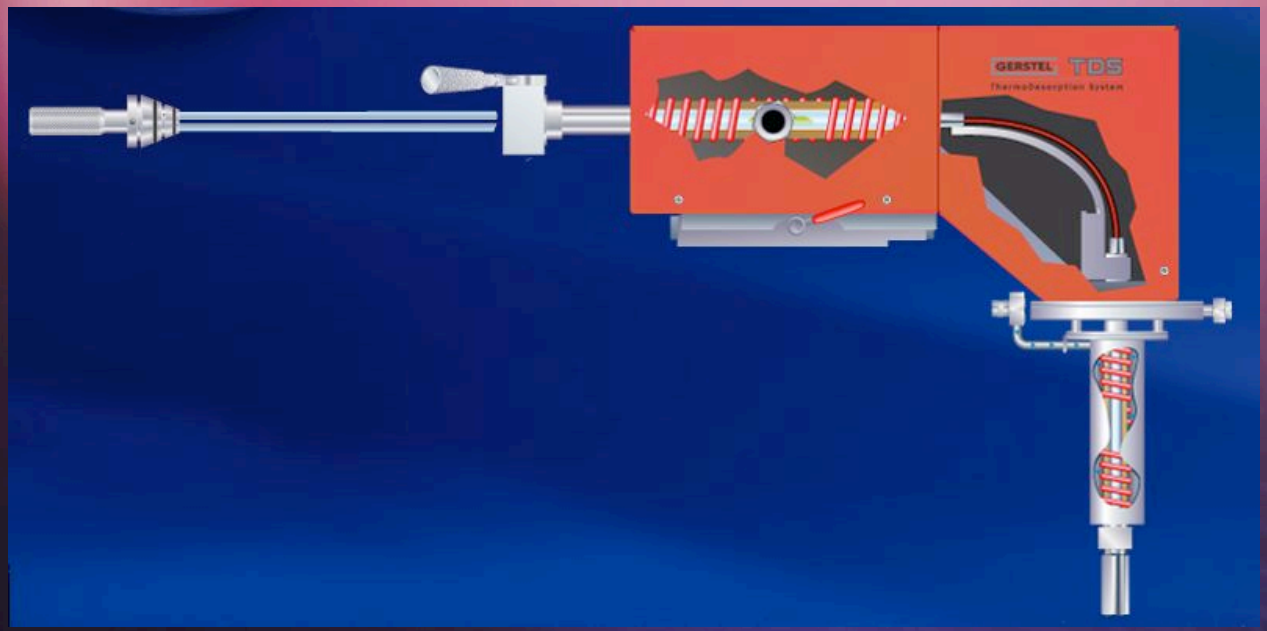
INTERPRETATION

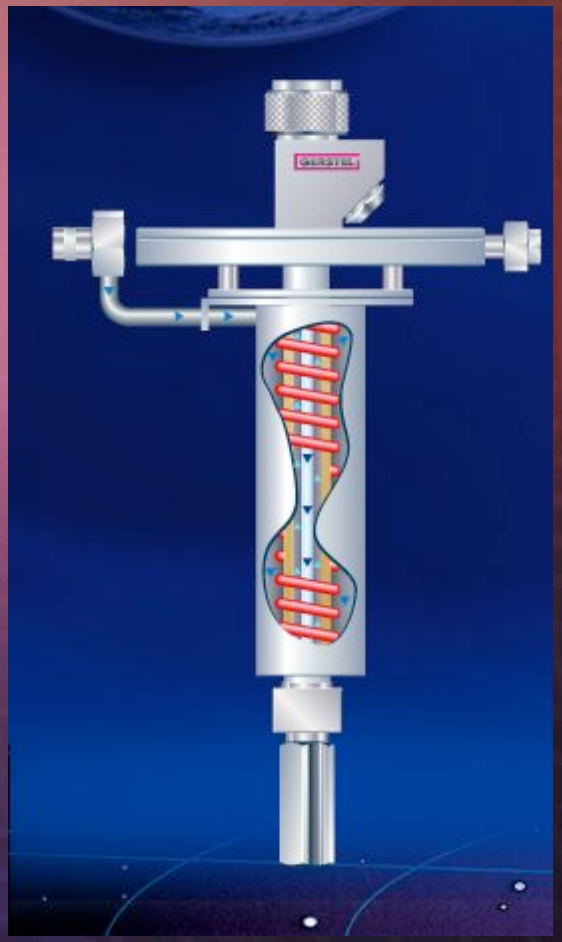
- identification
- quantification
- learnings

Current equipment

Current equipment (cont.)

- Gerstel TDS
- Gerstel CIS



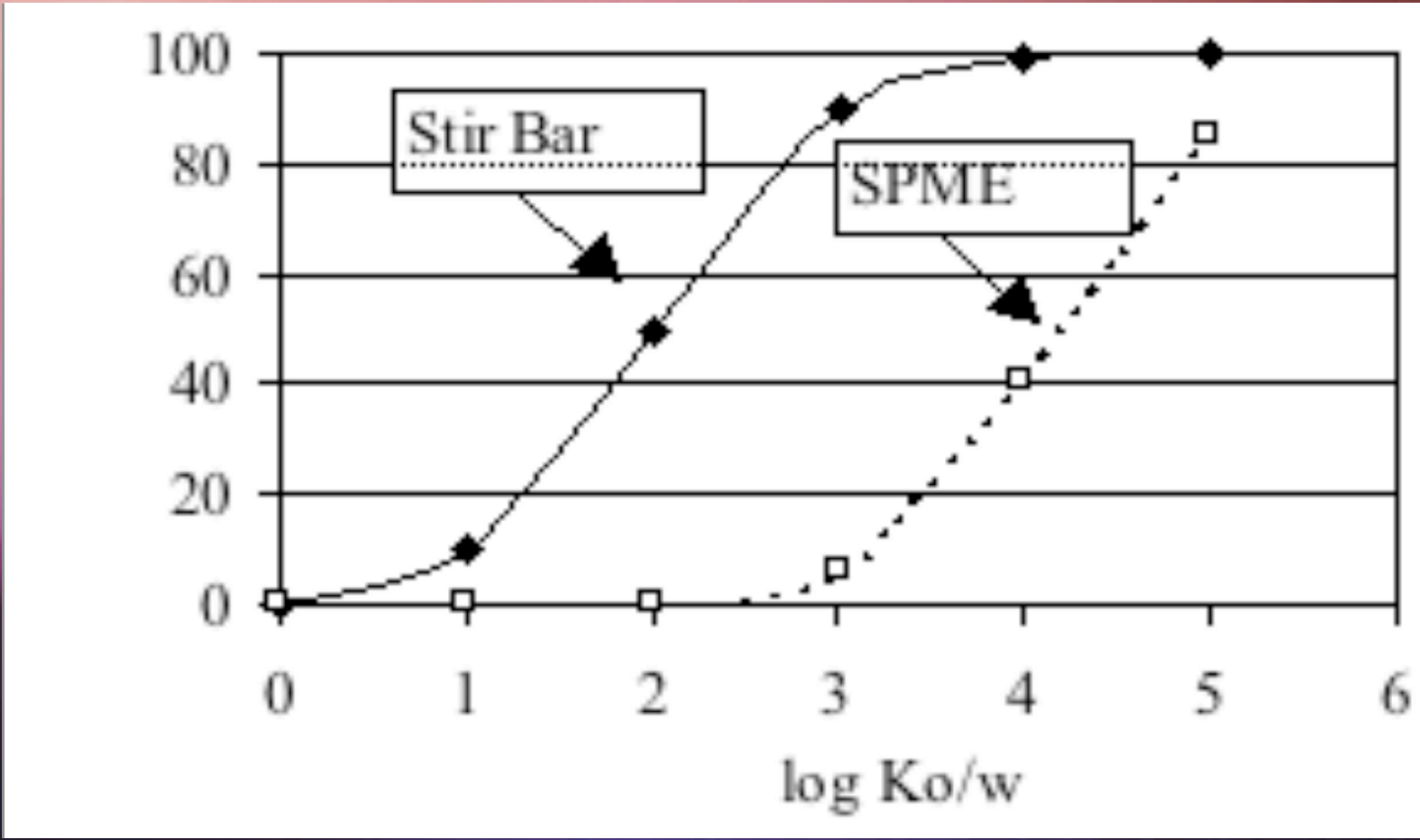


Twister

Method choice

- Dictated by:
  - Need for unbiased (i.e. fresh vs cooked)
  - Need for sensitivity (compared to static headspace)
  - Number of samples to analyze (>600 for the whole study)
  - Time available

Stir bar much more efficient than SPME



SPME work with MPS

Storage studies analysis

- Stability of flavor chemicals in a proprietary matrix under MAP conditions.
- Evolution of flavor profile of pasteurized flavored milk over shelflife

Stability of flavor chemicals under MAP

- 2 dozens of flavor compounds
  - Different chemical families
  - Different concentration
- Analyzed over 6 months as a function of:
  - time
  - Temperature
  - Chemical reactivity

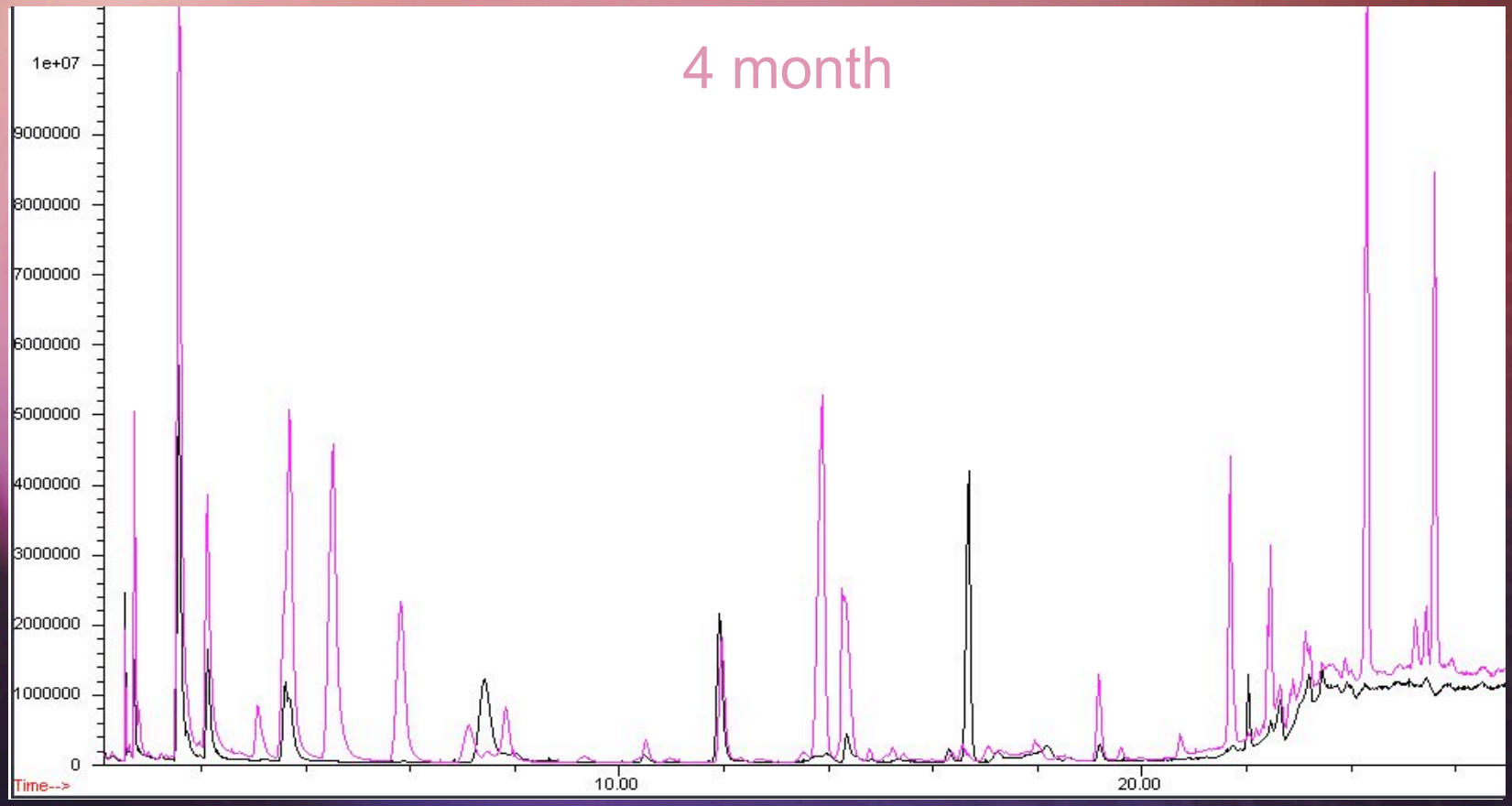
Stability of flavor chemicals under MAP (cont)

- Study set for 1200+ analyses not including
  - Standard curves
  - Development methodology
- Only doable with MPS

Stability of flavor chemicals under MAP (cont)

- Protocol
  - Sample (1 g in 20ml HS vial)
  - Equilibration 1 hr with PDMS/CAR/DVB at 50ºC
  - Injection 5 min
  - Analysis in SIM
  - Duplicate analysis

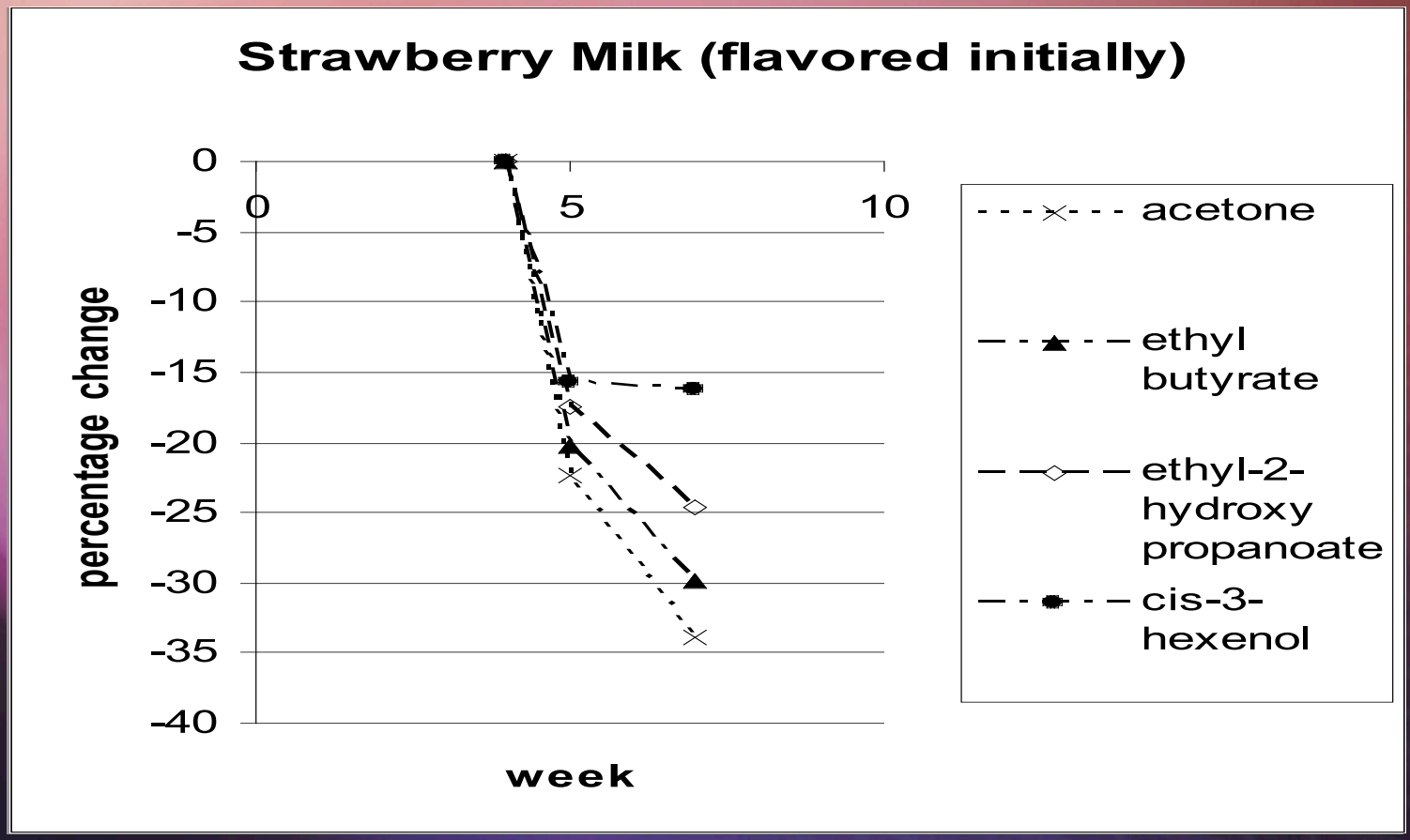
Total ions chromatograms



Extended shelflife of flavored milk

- Goal
  - Understand the shelflife of flavored milk
    - 4 different milks (including a control)
- Protocol (done in triplicate)
  - Equilibration of milk 45min at 45°C
  - Exposure of fiber (CARB/PDMS) 10min
  - Desorption 10 min at 250°C

Results – Strawberry Milk



Limitations of analytical method

- Review article from Nongonierma A. et al.
  - Competitive binding on fiber– quantification changes with other compounds adsorbed
  - Limited life of fiber (100 uses)
  - Fiber performance changes with time
  - Fibers vary in performance – (change fiber during study due to breakage)
- Implications
  - Data must be considered in terms of trends as opposed to individual data points
  - Not absolute values but relative values

Mechanisms of extraction of flavor compounds from foods, using adsorbents. Effects of various parameters. Nongonierma A., Cayot P., Le Quere JL., Springett M., Voilley A. (in press).

Theoretical Recovery

- $$\frac{m_{PDMS}}{m_o} = \frac{k_{PDMS/w} / É}{1 + k_{PDMS/w} / E}$$
- Where:
- m_{PDMS}/m_o = fraction of aroma compound isolated
- $k_{PDMS/w}$ = partition coefficient between fiber and food continuous phase
- m_o = total mass of analyte in food
- É = phase ratio e.g. V aqueous phase/ V extracting phase (PDMS)

Equation:

- Low Log P and low phase ratio characteristic of the method make isolation inefficient.
- E.g. SPME fiber generally has about 0.5 Él of phase
- Solution: stir bar method

Twister

- Advantages
  - Increased phase material
  - Increased surface area

- Type of extract
  - Headspace
  - Direct

Current/recent projects

- Flavor volatiles from crackers
- Flavor volatiles from flavor solutions
  - reconstituted
  - diluted
- Flavor volatiles from vegetable sauces
- Flavor volatiles from plant material
- Flavor volatiles in wines
- Flavor volatiles in mouth

Flavor volatiles from baked goods

- Goal
  - Determine presence of compounds of interest
  - Compare different extraction techniques
- Protocol (done in triplicate)

  50g of crackers in a jar (whole or ground)
  - Twister:
    - Twister placed on top of a Teflon mesh
    - Equilibration 1hr at 30ºC, 37ºC, 45ºC
    - Desorption splitless (+ cryofocusing) 5 min at 250ºC
  - Purge and trap:
    - 30 min at 45ºC, 40 ml / min
    - Desorption splitless (+ cryofocusing) 10 min at 250ºC

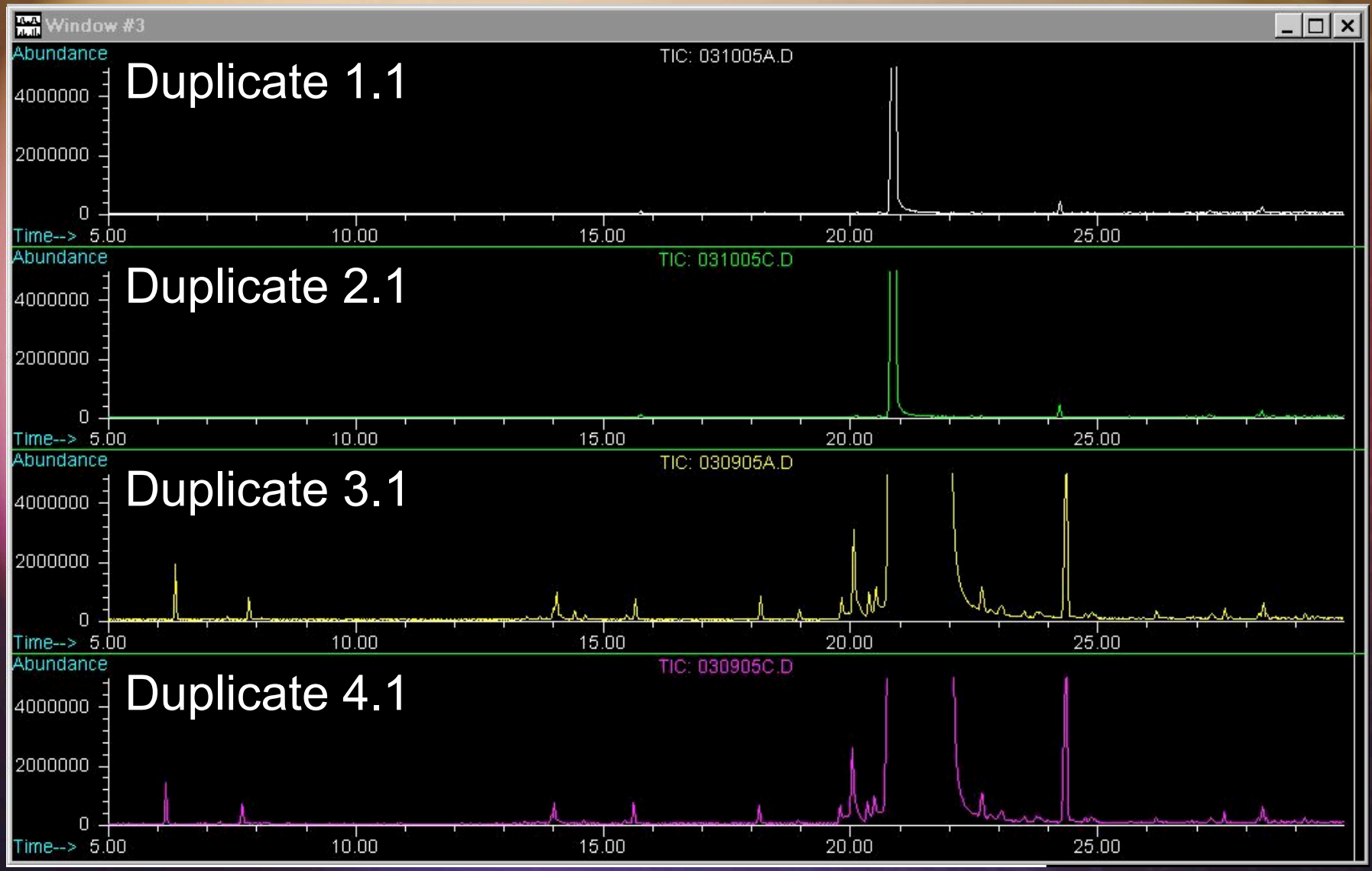
Twister
Purge&Trap
25000000
20000000
15000000
10000000
5000000
0
2-Methyl-butanal (ion 57)
Pentanal (ion 44)
Furfural
Furfuryl alcohol
p-Xylene
Heptanal
g-Butyrolactone
z(2)Heptenal
Benzaldehyde
2-Pentylfurane
Octanal
Limonene
E-2-Octenal
Nonanal
Phenylethylalcohol

37ºC
45ºC
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
2-Methyl-butanal (ion 57)
Pentanal (ion 44)
Furfural
Furfuryl alcohol
p-Xylene
Heptanal
g-Butyrolactone
z(2)heptenal
Benzaldehyde
2-Pentylfurane
Octanal
Limonene
E-2-octenal
Nonanal
Phenylethylalcohol

Flavor volatiles in flavor solutions

- Goal
  - Determine the difference in flavor compounds due to processing
- Protocol (done in duplicate)

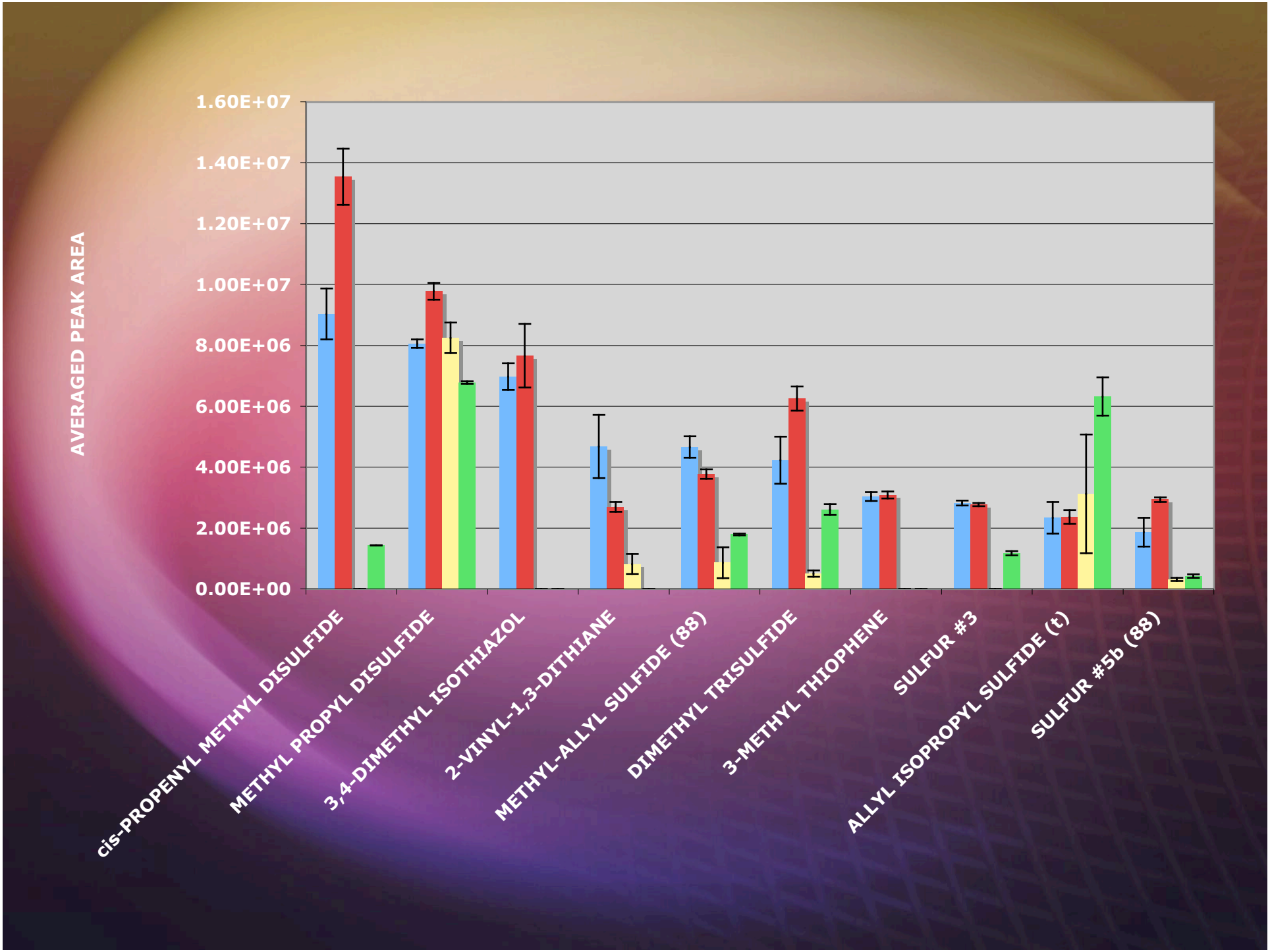
  10 ml of reconstituted beverage
  - Twister: exposure 45min at RT, desorbed splitless (+ cryofocusing) 5min at 250ºC
  - SPME-PDMS fiber (1 ml, 10min at RT), injection splitless at 250ºC

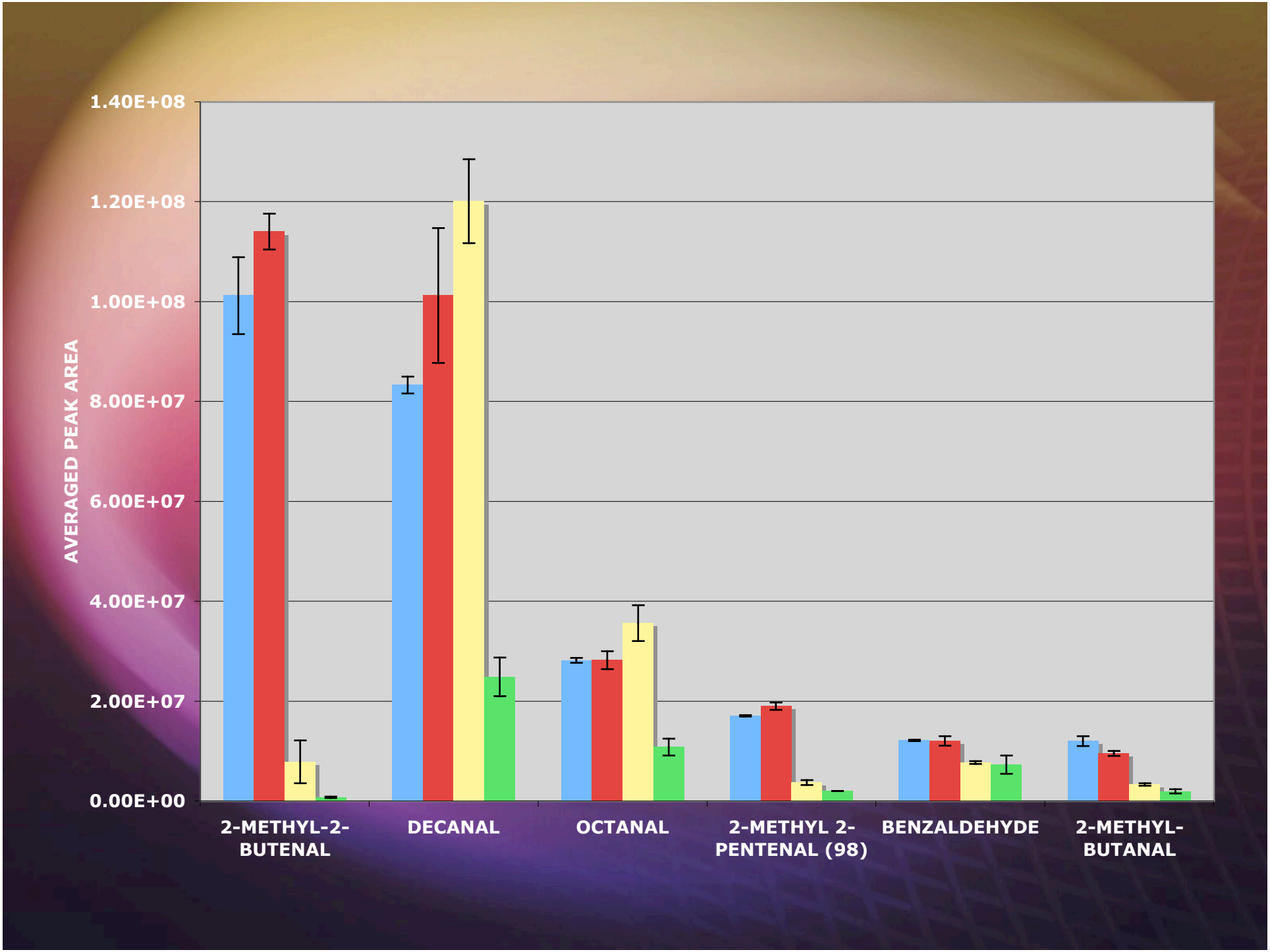

Window #3
Abundance
TIC: 031005A.D
Duplicate 1.1
4000000
2000000
0
Time--> 5.00
10.00
15.00
20.00
25.00
Abundance
TIC: 031005C.D
Duplicate 2.1
4000000
2000000
0
Time--> 5.00
10.00
15.00
20.00
25.00
Abundance
TIC: 030905A.D
Duplicate 3.1
4000000
2000000
0
Time--> 5.00
10.00
15.00
20.00
25.00
Abundance
TIC: 030905C.D
Duplicate 4.1
4000000
2000000
0
Time--> 5.00
10.00
15.00
20.00
25.00

Flavor volatiles in sauces

- Goal:

  Determine the
  - Difference in flavor profile
  - Origins
- Protocol (done in triplicate)
  - 100g sauce placed in a jar
  - Twister placed over sauce on a Teflon mesh
  - Exposure 30 min at 37ºC
  - Desorbed splitless (+ cryofocusing) 5 min at 250ºC


AVERAGED PEAK AREA
1.60E+07
1.40E+07
1.20E+07
1.00E+07
8.00E+06
6.00E+06
4.00E+06
2.00E+06
0.00E+00
cis-PROPENYL METHYL DISULFIDE
METHYL PROPYL DISULFIDE
3,4-DIMETHYL ISOTHIAZOL
2-VINYL-1,3-DITHIANE
METHYL-ALLYL SULFIDE (88)
DIMETHYL TRISULFIDE
3-METHYL THIOPHENE
SULFUR #3
ALLYL ISOPROPYL SULFIDE (t)
SULFUR #5b (88)


AVERAGED PEAK AREA
1.40E+08
1.20E+08
1.00E+08
8.00E+07
6.00E+07
4.00E+07
2.00E+07
0.00E+00
2-METHYL-2-BUTENAL
DECANAL
OCTANAL
2-METHYL 2-PENTENAL (98)
BENZALDEHYDE
2-METHYL-BUTANAL

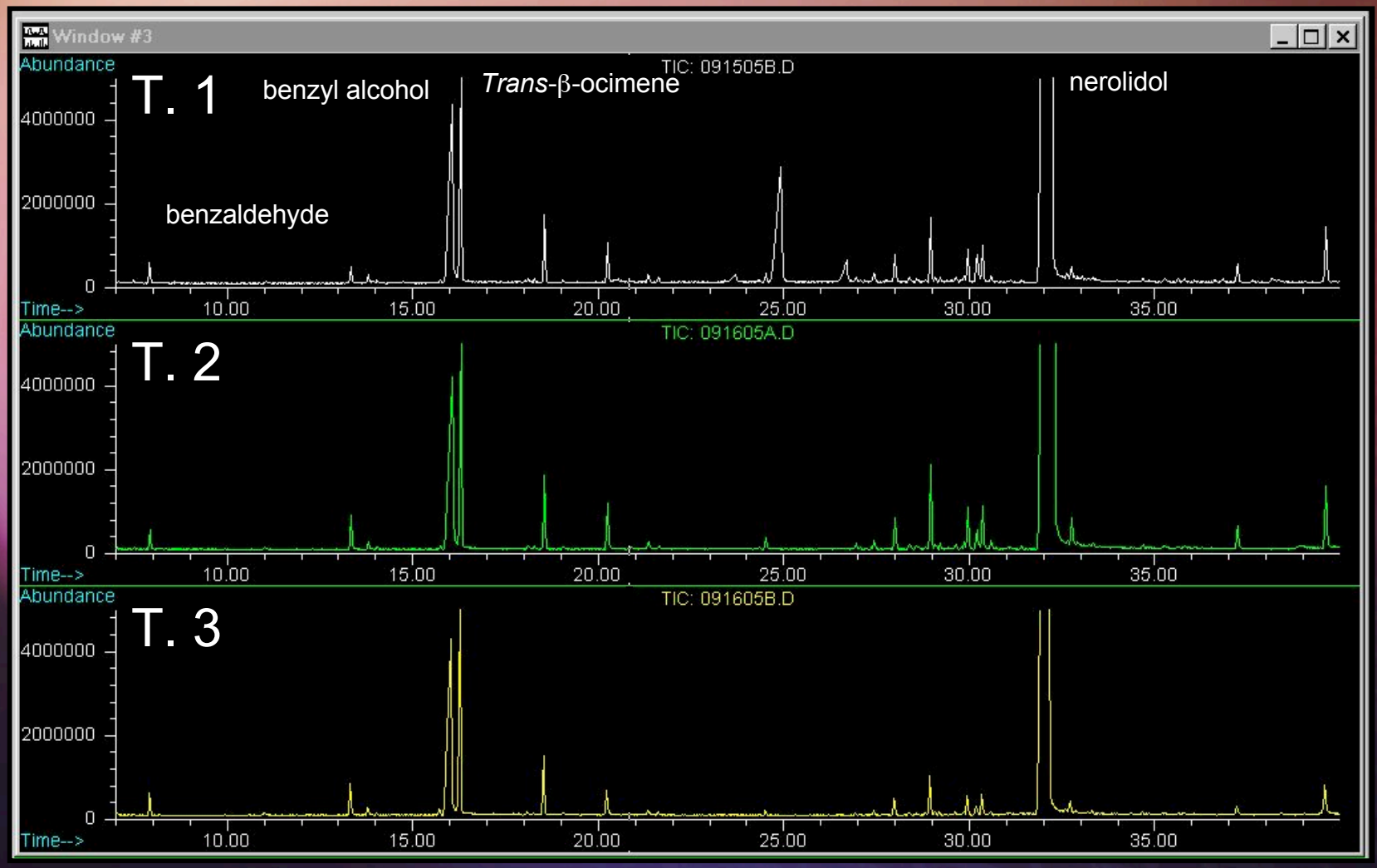
Flavor volatiles in plants

- Goal

  determine volatile components of flowers

- Protocol
  - Twisters (10) placed in round bottom flask
  - Round bottom flask placed over bud before bloom
  - Twisters exposed 12 hrs at 15ºC
  - Desorbed splitless (+ cryofocusing) 5 min at 250ºC

Triplicates of flower extract

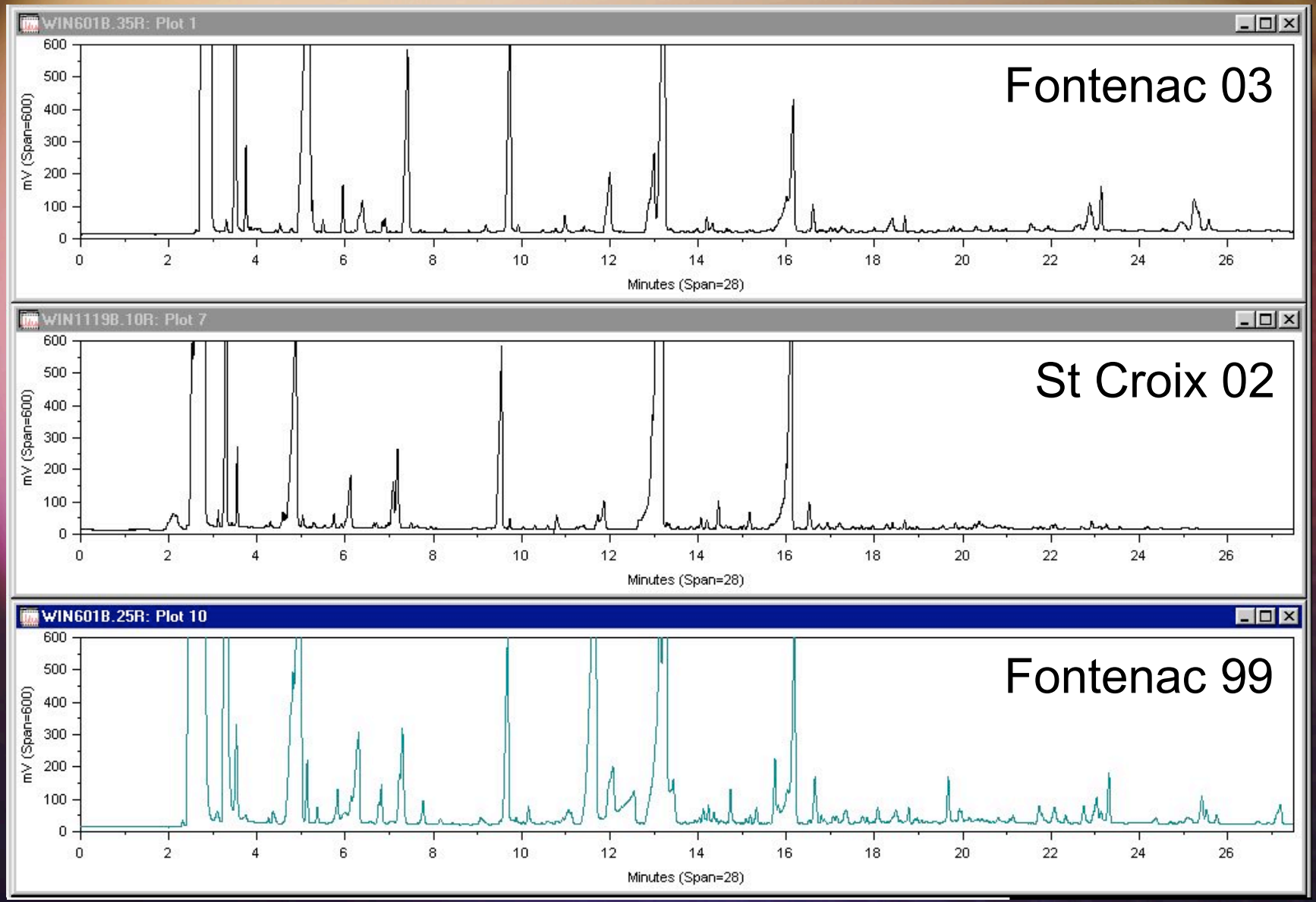


Flavor volatiles in wines

- Goal:

  determine differences in flavor volatiles between wine and correlate to sensory profile, plant variety.

- Protocol:
  - Twister placed into 10 ml wine
  - Equilibrated for 1.5hr at room temperature
  - Desorbed splitless (+ cryofocusing) 10 min at 270°C


WIN601B.35R: Plot 1
Fontenac 03
mV (Span=600)
Minutes (Span=28)
WIN1119B.10R: Plot 7
St Croix 02
mV (Span=600)
Minutes (Span=28)
WIN601B.25R: Plot 10
Fontenac 99
mV (Span=600)
Minutes (Span=28)

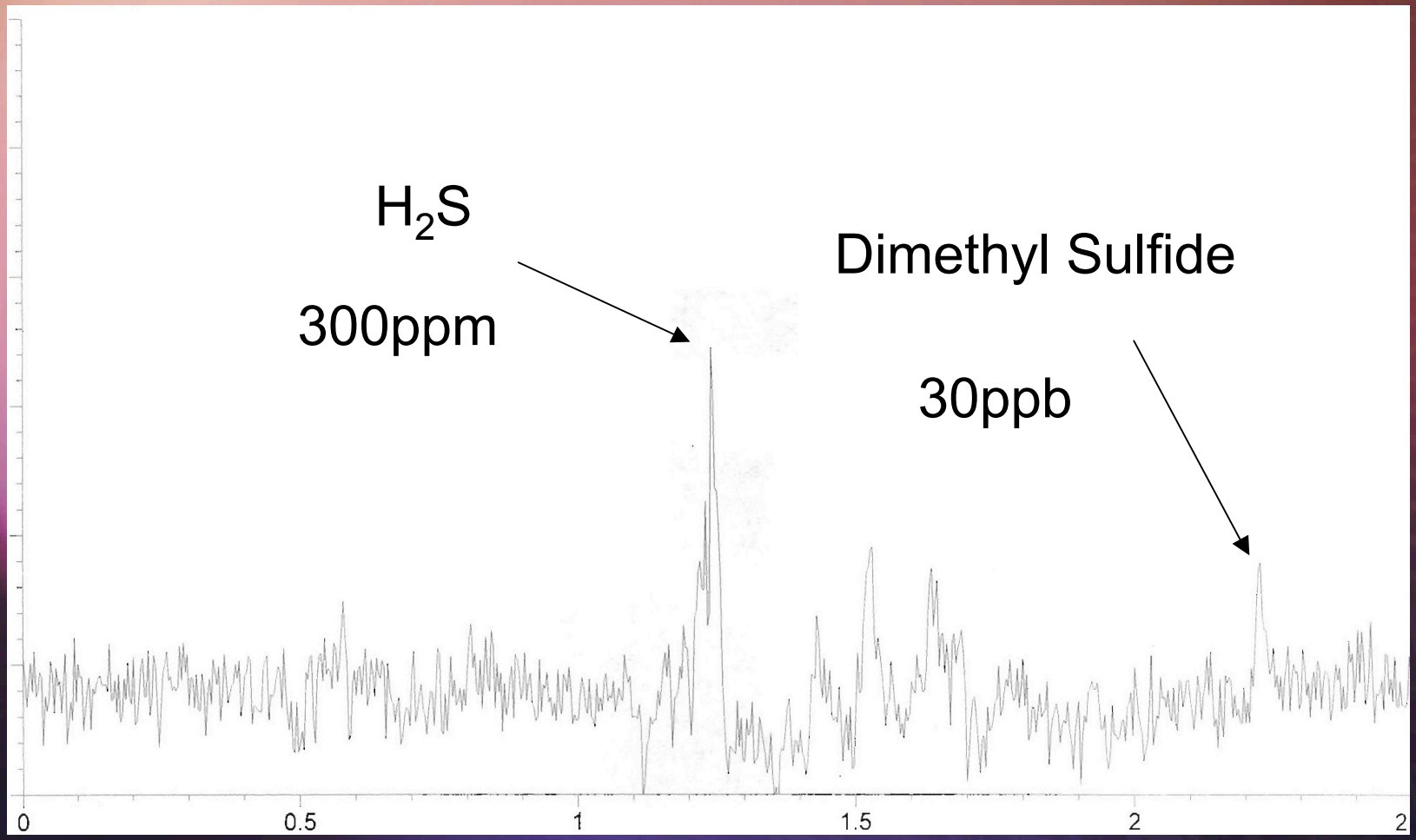
Flavor volatiles in mouth

- Goal

  understand the effect of some particular mouthwash components on the decrease of sulfur compounds responsible for bad breath

- Protocol (in triplicate)
  - Twister placed in mouth for 5 mins
  - Dried (KimWhip)
  - desorbed in splitless (+ cryofocusing) 5 min at 190°C

Analysis of sulfur compounds



Summary

- Twister: big improvement
  - More phase, better sensitivity
  - Easier, more reproducible, more stable
- Limitations?
  - fat matrices
  - carry over
  - cryofocusing

Summary

- The Automatic Liner Exchange: ALEX

Acknowledgments
Questions

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Deena Strohman