Flavor analysis and research at the University of Minnesota

Jean-Paul Schirlé-Keller
jpsk@spectraflavor.com
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

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

- injection
- separation
- detection

- 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 50°C
  - Injection 5 min
  - Analysis in SIM
  - Duplicate analysis
Total ions chromatograms

4 month
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

Strawberry Milk (flavored initially)

-40
-35
-30
-25
-20
-15
-10
-5
0

week

percentage change

- - - - acetone
- - - ethyl butyrate
- - ethyl-2-hydroxy propanoate
- - - cis-3-hexenol
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
Theoretical Recovery

\[ \frac{m_{PDMS}}{m_o} = \frac{k_{PDMS/w} / \dot{E}}{1 + k_{PDMS/w} / \dot{E}} \]

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
- \( \dot{E} \) = 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 30°C, 37°C, 45°C
    ♦ Desorption splitless (+ cryofocusing) 5 min at 250°C
  ♦ Purge and trap:
    ♦ 30 min at 45°C, 40 ml / min
    ♦ Desorption splitless (+ cryofocusing) 10 min at 250°C
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

Twister
Purge&Trap

37°C
45°C
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
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 37°C
  ♦ Desorbed splitless (+ cryofocusing) 5 min at 250°C
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 15°C
  - Desorbed splitless (+ cryofocusing) 5 min at 250°C
Triplicates of flower extract

T. 1
- benzyl alcohol
- Trans-β-ocimene
- benzaldehyde
- nerolidol

T. 2

T. 3
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 270ºC
Fontenac 03

St Croix 02

Fontenac 99
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

H$_2$S
300ppm

Dimethyl Sulfide
30ppb
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
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Questions

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