Sensory Relevance of Volatile Organic Sulfur Compounds in Food

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Major topics of the presentation

Overview
- Chemical classes
- Occurrence
- Analytical methods

Key odorants
- Sensory relevance
- Structure - activity
- Flavor simulation

Food products
- Natural
- Fermented
- Processed
Major classes of sulfur compounds

- **Sulfides** (~ 440)
  - Mono (55)
  - Di (95)
  - Tri (25)
  - Others (265)

- **Thiazoles** (100)
  - Thiane (50)
  - Thiocyanate (45)
  - Thiolane (25)
  - Dithiazine (20)
  - Others (125)

- **Thiophenes** (100)

- **Thiols** (60)

Total: ~ 700 sulfur compounds ≅ 10% of volatiles listed in TNO compilation
Key odorants: Thiols in natural products

Grapefruit
Sulfury, catty
$O_x = 0.00002 \ \mu g/L \ H_2O$  
(Demole et al., 1982)

(\textit{R})-1-p-Menthene-8-thiol

Onion
Sulfury, onion, meaty
$O_x = 0.04 \ \mu g/L \ H_2O$  
(Widder et al., 2000)

3-Mercapto-2-methylpentan-1-ol
(2\textit{R},3\textit{S}) / (2\textit{S},3\textit{R})

Blackcurrant, olive oil
Sulfury, catty
$O_x = 0.001 \ \mu g/L \ H_2O$  
(Rigaud et al., 1986
Guth & Grosch, 1991)

4-Methoxy-2-methyl-2-butanethiol

Buchu leaf oil
Sulfury, catty

(Sundt et al., 1971)

8-Mercapto-p-mentane-3-one
\textit{trans}-(1\textit{S},4\textit{S}) / \textit{cis}-(1\textit{S},4\textit{R})
Key odorants: Thiols by thermal processing

3-Mercapto-2-buten-1-thiol

Beer, coffee
Sulfury, catty
$O_x = 0.0003 \, \mu g/L \, H_2O$

(Kuroiwa & Hashimoto, 1961; Holscher et al., 1990)

3-Mercapto-3-methylbutyl formate

Coffee, beer
Sulfury, catty
$O_x = 0.003 \, \mu g/L \, H_2O$

(Holscher et al., 1990; Schieberle, 1991)

2-Methyl-3-furanthiol

Meat, coffee
Sulfury, meaty
$O_x = 0.007 \, \mu g/L \, H_2O$

(Gasser & Grosch, 1988; Holscher et al., 1990)

2-Furfurylthiol

Coffee, meat, ...
Sulfury, coffee-like
$O_x = 0.01 \, \mu g/L \, H_2O$

(Reichstein & Staudinger, 1926; Mottram, 1985)
Occurrence of key odorants: Sulfides

Shellfish (cooked)  Shiitake mushroom  Meat flavors, chocolate  Passion fruit  Garlic

Potato (boiled)  White truffle  Vegetables  Onion (raw)  Onion (boiled)
Odor quality and threshold value: Sulfides

- **Roasty**
  - 1 x 10^{-11} \mu g/L
  - (Kubota et al., 1991)

- **Sulfury, meaty**
  - 0.00002 \mu g/L
  - (Buttery et al., 1982)

- **Sulfury, roasty**
  - 0.04 \mu g/L
  - (Mulders, 1976)

- **Sulfury, cabbage-like**
  - 0.006 \mu g/L
  - (Milo, 1995)

- **Cooked potato-like**
  - 0.2 \mu g/L
  - (Buttery et al., 1971)

- **Sulfury**
  - 0.3 \mu g/L
  - (Sloot & Harkes, 1975)

- **Sulfury, onion**
  - 2 \mu g/L
  - (Boelens & van Gemert, 1993)

- **Sulfury, fruity**
  - 7 \mu g/L
  - (Takeoka et al., 1989)
Key odorants: Thiazoles, thiophenes, and others

1. Tomato: 3.0
2. Leek: 7.0
3. Fried onion: 1.2
4. Watercress: 1.6
5. Chopped cabbage: 1.3
6. Leek: 1.3
7. Horseradish: 1.0
8. Radish: 0.1
## Sensory Directed Chemical Analysis

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aroma extraction</td>
<td>Various</td>
<td>Authentic aroma note</td>
</tr>
<tr>
<td>GC-Olfactometry</td>
<td>Sniffing, Charm, AEDA, ...</td>
<td>Screening of odorants</td>
</tr>
<tr>
<td>Identification</td>
<td>GC-MS, AED, RI, specific detectors, ...</td>
<td>Structure of odorant</td>
</tr>
<tr>
<td>Quantification</td>
<td>Internal standard, IDA</td>
<td>Concentration in food</td>
</tr>
<tr>
<td>Sensory evaluation</td>
<td>Triangle test, profiling, various matrices, ...</td>
<td>Odor threshold + quality Masking, sens. impact</td>
</tr>
<tr>
<td>Validation</td>
<td>Recombination</td>
<td>Flavor simulation</td>
</tr>
</tbody>
</table>

(Acree, 1993; Grosch, 1994; Schieberle, 1995; Blank, 1996)
GC-Sniffing / GC-Olfactometry

Evers et al. (1976)  
Withcombe & Mussinan (1988)  
Gasser & Grosch (1988)  
Gasser & Grosch (1990)  
Holscher et al. (1990)  
Gasser & Grosch (1991)  
...  

Synthesis  GC-MS  
Tuna fish  GC-O, GC-MS  
Beef  GC-O  
Chicken  GC-O, GC-MS  
Coffee  GC-O  
Pork  GC-O
Dilution techniques: CHARM and AEDA

Serial Dilution

(Acree et al., 1984; Ullrich & Grosch, 1987)
Sulfur compounds in grapefruit

- Sulfury, catty
  (0.00002 µg/L H₂O)

- Sulfury, catty
  (0.0001 µg/L H₂O)

- Cooked potato-like
  (0.2 µg/L H₂O)

(Demole et al., 1982)

(Buettner & Schieberle, 1999)
Isolation and selective enrichment of thiols with p-hydroxymercuribenzoate

(Darriet et al., 1995)
Isolation and selective enrichment of thiols by covalent chromatography

(Full & Schreier, 1995)
Sensory relevance: Odor Activity Value

\[ \text{OAV} = \frac{C_x}{T_x} \]

- \(C_x\): Concentration
- \(T_x\): Threshold value

Thresholds:
- Odor (orthonasal)
- Aroma (retronasal)

Perception
Recognition

Solvent: Air, Water, Oil, Food

Rothe & Thomas (1963)
Guadagni et al. (1966)
Acree et al. (1984)
Buttery et al.
Grosch et al.
Schieberle et al.

😊: Relative importance of individual odorants estimated

😔: Interactions remain unknown

→ Flavor recombination studies
Threshold values: A very critical step

Odor
orthonasal (through the nose)

Aroma
retronasal (in the mouth)

Perception
different from solvent

Recognition
characteristic note perceived

Solvents:

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Air (ng/L)</th>
<th>Water (µg/L)</th>
<th>Model (µg/L)</th>
<th>Food (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0002</td>
<td>0.001</td>
<td>n.d.</td>
<td>0.045 (oil)</td>
</tr>
<tr>
<td></td>
<td>n.d.</td>
<td>0.0001</td>
<td>0.001 (10% EtOH)</td>
<td>0.003 (wine)</td>
</tr>
<tr>
<td></td>
<td>0.001 (10% EtOH)</td>
<td>0.27 (starch)</td>
<td>0.05/0.2 (oil)</td>
<td></td>
</tr>
</tbody>
</table>

OAV = \frac{C_x}{T_x}
**Effect of the threshold value: Roasted sesame**

<table>
<thead>
<tr>
<th>Flavor compound</th>
<th>Concentration (µg/kg)</th>
<th>Odor thresholds (µg/kg oil; water)</th>
<th>OAV Oil</th>
<th>OAV Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Acetyl-1-pyrroline</td>
<td>30</td>
<td>0.1</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>2-Furfurylthiol</td>
<td>54</td>
<td>0.4</td>
<td>135</td>
<td>5400</td>
</tr>
<tr>
<td>2-Phenylethylthiol</td>
<td>6</td>
<td>0.05</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>Furaneol</td>
<td>2510</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>2-Ethyl-3,5-dimethylpyrazine</td>
<td>53</td>
<td>3</td>
<td>18</td>
<td>530</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>270</td>
<td>19</td>
<td>14</td>
<td>90</td>
</tr>
<tr>
<td>(E,E)-2,4-Decadienal</td>
<td>89</td>
<td>180</td>
<td>&lt;1</td>
<td>445</td>
</tr>
</tbody>
</table>

(Schieberle, 1996)
Sulfur compounds in natural products

Tomato, olive oil, basil

Odorants: Chemical structure
Sensory properties
Flavor recombination
Catty odorants
Odor characteristics of 2-isobutylthiazole and its impact on the overall tomato flavor

Viani et al., 1969
- In pure form: Green, similar to tomato leafs
- First identified in tomato fruit (500 kg)

Kazeniac & Hall, 1970
- In water: Spoiled wine-like, horseradish-like
- Threshold of 2-3 µg/kg water
- Added to canned tomato (juice / paste): More intense fresh tomato note
- Blended out harsh notes
- Improved the mouth-feel
- Effective at 25-50 µg/kg level
### Key odorants of fresh tomato

<table>
<thead>
<tr>
<th>Flavor compound</th>
<th>Concentration (µg/kg)</th>
<th>Odor threshold (µg/kg water)</th>
<th>OAV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Z)-3-Hexenal</td>
<td>12000</td>
<td>0.25</td>
<td>50000</td>
</tr>
<tr>
<td>Hexanal</td>
<td>3100</td>
<td>4.5</td>
<td>630</td>
</tr>
<tr>
<td>β-Ionone</td>
<td>4</td>
<td>0.007</td>
<td>630</td>
</tr>
<tr>
<td>1-Penten-3-one</td>
<td>520</td>
<td>1</td>
<td>500</td>
</tr>
<tr>
<td>β-Damascenone</td>
<td>1</td>
<td>0.002</td>
<td>500</td>
</tr>
<tr>
<td>3-Methylbutanal</td>
<td>27</td>
<td>0.2</td>
<td>130</td>
</tr>
<tr>
<td>(E)-2-Hexenal</td>
<td>270</td>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>2-Isobutylthiazole</td>
<td>36</td>
<td>3.5</td>
<td>10</td>
</tr>
<tr>
<td>1-Nitro-2-phenylethane</td>
<td>17</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Buttery et al., 1989)
Key odorants of olive oil (Spain)

<table>
<thead>
<tr>
<th>Flavor compound</th>
<th>Concentration (µg/kg)</th>
<th>Odor Threshold (µg/kg oil)</th>
<th>OAV</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Methoxy-2-methyl-2-butanethiol</td>
<td>1.8</td>
<td>0.045</td>
<td>40</td>
</tr>
<tr>
<td>(Z)-3-Hexenal</td>
<td>53</td>
<td>2.8</td>
<td>19</td>
</tr>
<tr>
<td>Ethyl 2-methylbutyrate</td>
<td>14</td>
<td>0.75</td>
<td>19</td>
</tr>
<tr>
<td>(Z)-2-Nonenal</td>
<td>10</td>
<td>0.6</td>
<td>17</td>
</tr>
<tr>
<td>Ethyl 3-methylbutyrate</td>
<td>7.9</td>
<td>0.75</td>
<td>11</td>
</tr>
<tr>
<td>Ethyl cyclohexanoate</td>
<td>4.3</td>
<td>0.38</td>
<td>11</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>6680</td>
<td>1050</td>
<td>6.4</td>
</tr>
<tr>
<td>Hexanal</td>
<td>390</td>
<td>74</td>
<td>5.3</td>
</tr>
<tr>
<td>(Z)-3-Hexenyl acetate</td>
<td>3380</td>
<td>750</td>
<td>4.5</td>
</tr>
<tr>
<td>3-Methylbutanol</td>
<td>900</td>
<td>225</td>
<td>4.0</td>
</tr>
</tbody>
</table>

(Guth & Grosch, 1991; 1993)
Recombination studies: Olive oil (Spain)

Model (Reiners & Grosch, 1998)

Similarity: 2.7 ± 0.3 (21 odorants)

Oil
Model

Pungent
Catty
Fruity
Fatty
Green

(Reiners & Grosch, 1998)
Effect of odorants on overall flavor
- Olive oil (Spain) -

Sample | Similarity
--- | ---
S0 | 2.7
S1 | 2.7
S2 | 2.4
S3 | 2.3
S4 | 2.3
S5 | 0.9

Samples S0 to S5 represent different mixtures of odorants:
- S0: Model mixture (21 odorants)
- S1: No acetaldehyde / propanal
- S2: No acetic acid
- S3: No 3-/2-methylbutanal
- S4: No ethyl 2-/3-methylbutyrate
- S5: No 4-methoxy-2-methyl-2-butanthiol

(Reiners & Grosch, 1998)
## Key odorants and sensory profiling - Fresh basil -

<table>
<thead>
<tr>
<th>Flavor compound</th>
<th>OAV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Z)-3-Hexenal</td>
<td>413000</td>
</tr>
<tr>
<td>1,8-Cineol</td>
<td>246000</td>
</tr>
<tr>
<td>4-Mercapto-4-methyl-2-pentanone</td>
<td>83000</td>
</tr>
<tr>
<td>Linalool</td>
<td>40000</td>
</tr>
<tr>
<td>4-Allyl-1,2-dimethoxybenzene</td>
<td>9900</td>
</tr>
<tr>
<td>Eugenol</td>
<td>8900</td>
</tr>
<tr>
<td>α-Pinene</td>
<td>90</td>
</tr>
</tbody>
</table>

(Guth & Murgoci, 1997)
Recombination studies : Fresh basil aroma

<table>
<thead>
<tr>
<th>Model mixture</th>
<th>Similarity</th>
<th>OAV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete mixture (11 odorants)</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Compounds ommitted :</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eugenol</td>
<td>0.7</td>
<td>8900</td>
</tr>
<tr>
<td>(Z)-3-Hexenal</td>
<td>1.0</td>
<td>413000</td>
</tr>
<tr>
<td>α-Pinene</td>
<td>1.3</td>
<td>90</td>
</tr>
<tr>
<td>4-Mercapto-4-methyl-2-pentanone</td>
<td>1.6</td>
<td>83000</td>
</tr>
<tr>
<td>Linalol</td>
<td>1.8</td>
<td>40000</td>
</tr>
<tr>
<td>1,8-Cineol</td>
<td>1.9</td>
<td>246000</td>
</tr>
</tbody>
</table>

(Guth & Murgoci, 1997)
Structure - activity relationship: ‘Catty’

(Thresholds in µg/L water)
Molecular features determining the ‘catty’ odor

Results:
• Tertiary mercapto amyl substructure
• Keto group is not essential, might be in \( \alpha \)- or \( \beta \)-position to SH
• SH to C=O distance is 2-4 Å

(Polak et al., 1988)

Sensory evaluation:
• Tested in a confusion matrix
• Factor correspondence analysis
• Sensory panel (n = 15)
Sulfur compounds in fermented products

Wines:
- White (Sauvignon, Scheurebe)
- Red (Bordeaux)

Odorants:
- Chemical structure
- Sensory properties (‘catty’)
- Stereochemistry
- Precursors
- Flavor recombination
Sulfur compounds in wine: Sauvignon blanc

4-Mercapto-4-methyl-2-pentanone

- O = 0.1 ng/L water
- O = 1.1 ng/L 10% ethanol
- O = 1.4 ng/L 10% ethanol sucrose (100 g/L)
- O = 3.3 ng/L white/red wine

- C = 12-34 ng/L white wine

(Bouchilloux et al., 1996)

(Darriet et al., 1993)

(Darriet et al., 1995)

C = 0 ng/L white wine No typical aroma
C = 9 ng/L white wine Weak typical note
C = 18 ng/L white wine Typical aroma
C = 34 ng/L white wine Very typical note
Further sulfur compounds in Sauvignon blanc

3-Mercaptohexyl acetate  
Passion fruit-like  
O = 2.3 ng/L water  
O = 4.3 ng/L 10% EtOH  
(Tominaga et al., 1996)

3-Mercapto-1-hexanol  
Passion fruit, grapefruit  
O = 17 ng/L water  
O = 60 ng/L 10% EtOH  
(Tominaga et al., 1998)

4-Mercapto-4-methyl-2-pentanol  
Citrus peel-like  
O = 20 ng/L water  
O = 55 ng/L 10% EtOH

3-Mercapto-3-methyl-1-butanol  
Cooked leek-like  
O = 1300 ng/L water  
O = 1500 ng/L 10% EtOH
Sensory impact of sulfur compounds in Sauvignon blanc

(Tominaga et al., 1998)
$S$-Cysteine conjugates as precursors of thiols in Sauvignon blanc

Alcoholic fermentation ($\beta$-lyase of yeast)

Thiols released (enhanced Sauvignon blanc aroma)

(Tominaga et al., 1998)
Use of the β-lyse activity of yeast - Application to flavour generation -

(Tominaga et al., 1998)

(Bel Rhlid & Matthey-Doret., 1998)
Use of the yeast β-CS-lyse activity in flavour generation

(Bel Rhlid & Matthey-Doret., 1998)
Sulfur compounds in white wine: Scheurebe

- **4-Mercapto-4-methyl-2-pentanone**
  - Sulfury, catty

- **Dimethyl sulfide**
  - Sulfury, tomato-like

- **Dimethyl trisulfide**
  - Sulfury, cabbage-like

- **3-(Methylthio)-1-propanol**
  - Sulfury, cabbage-like

(Guth, 1997)
Key odorants in Scheurebe wine

(Guth, 1997)
Sensory impact of odorants in the Scheurebe wine

<table>
<thead>
<tr>
<th>Model mixture</th>
<th>Similarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete mixture (42 odorants)</td>
<td>3.0</td>
</tr>
<tr>
<td>Compound omitted:</td>
<td></td>
</tr>
<tr>
<td>4-Mercapto-4-methyl-2-pentanone</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*(Guth, 1997)*
Sulfur compounds in Bordeaux red wines

3-Mercaptohexyl acetate
- Passion fruit-like
- O = 2.3 ng/L water
- C = 1-200 ng/L wine

3-Mercapto-1-hexanol
- Grapefruit-like
- O = 17 ng/L water
- C = 0.01-5 µg/L wine

3-Mercapto-2-methylpropanol
- Broth-like, sweaty
- O = 3000 ng/L water
- C = 1-70 µg/L wine

(Bouchilloux et al., 1998)
**Stereochemistry of 3-mercaptopropanoic acid**

Brothy, sweaty

3-7 µg/L (water)  35-40 µg/L
20-27 µg/L (model) 120-130 µg/L

- Young red wines: 25-70 µg/L
- Aged red wines: 1-4 µg/L
- White wines: 1-2 µg/L

(Bouchilloux et al., 2000)
Sulfur compounds in red wine (*Vitis labrusca*)

- **3-(Methylthio)-1-propanol**: Sulfury, cabbage-like
- **trans-2-Methylthiophan-3-ol**: Garlic-like
- **4-Mercapto-2,5-dimethyl 3(2H)-thiophenone**: Sulfury, sweet, fruity

*(Guedes de Pinho et al., 1997)*
Sulfur compounds in processed foods

Food: Meat (stewed beef)  Coffee (brew)

Odorants: Chemical structure  Sensory properties  Flavor recombination
## Key odorants found in stewed meat juice

<table>
<thead>
<tr>
<th>Flavor compound</th>
<th>Concentr. (µg/kg)</th>
<th>Odor threshold (µg/kg water)</th>
<th>OAV Beef</th>
<th>OAV Pork</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Beef</td>
<td>Pork</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanethiol</td>
<td>300</td>
<td>500</td>
<td>0.2</td>
<td>1560</td>
</tr>
<tr>
<td>12-Methyltridecanal</td>
<td>52</td>
<td>&lt;0.5</td>
<td>0.1</td>
<td>520</td>
</tr>
<tr>
<td>Furaneol</td>
<td>8000</td>
<td>2700</td>
<td>25</td>
<td>320</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>6400</td>
<td>1500</td>
<td>25</td>
<td>256</td>
</tr>
<tr>
<td>Methional</td>
<td>13</td>
<td>23</td>
<td>0.2</td>
<td>65</td>
</tr>
<tr>
<td>(E,E)-2,4-Decadienal</td>
<td>12</td>
<td>10</td>
<td>0.2</td>
<td>60</td>
</tr>
<tr>
<td>3-Methylbutanal</td>
<td>10</td>
<td>21</td>
<td>0.4</td>
<td>25</td>
</tr>
<tr>
<td>Sotolone</td>
<td>5</td>
<td>3</td>
<td>0.3</td>
<td>17</td>
</tr>
<tr>
<td>Hexanal</td>
<td>72</td>
<td>15</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>2x10^5</td>
<td>3x10^5</td>
<td>3x10^4</td>
<td>6</td>
</tr>
<tr>
<td>2-Furfurylthiol</td>
<td>0.5</td>
<td>0.6</td>
<td>0.12</td>
<td>4</td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Guth & Grosch, 1994; 1995)
Sensory profiling of stewed meat flavor

(Guth & Grosch, 1995)
Effect of odorants on overall flavor: Stewed beef

(Guth & Grosch, 1994)

(Samples)

S1
S3
S5
S7

0.5
1.5
2.5
3.5

Similarity

Model mixture (n=15)
No 2-furfurylthiol
No acetaldehyde
No sotolone
No acetic acid
No 12-methyltridecanal
No furaneol
No methanethiol

(Guth & Grosch, 1994)
## Interaction of odorants: Stewed beef

<table>
<thead>
<tr>
<th>Flavor compound</th>
<th>Model A</th>
<th>Model B</th>
<th>Model C</th>
<th>Model D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanethiol</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Furaneol</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>12-Methyltridecanal</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Sotolone</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>2-Furfurylthiol</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Methional</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Butyric acid</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>((E,E))-2,4-Decadienal</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Diacetyl</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>3-Methylbutanal</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

**Similarity:**

|       | 0 | 2 | 2.5 | 3   |

*(Guth & Grosch, 1994)*
Some odorants detected in coffee by GC-olfactometry

(Holscher et al., 1990-1992; Blank et al., 1991-1992)
### Key odorants found in Arabica coffee brew (1)

<table>
<thead>
<tr>
<th>Flavor compound</th>
<th>Concentration (µg/kg)</th>
<th>Odor threshold (µg/kg water)</th>
<th>OAV (x10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Furfurylthiol</td>
<td>1680</td>
<td>0.01</td>
<td>168</td>
</tr>
<tr>
<td>3-Methyl-2-buten-1-thiol</td>
<td>8.6</td>
<td>0.0003</td>
<td>28.7</td>
</tr>
<tr>
<td>Methanethiol</td>
<td>4700</td>
<td>0.2</td>
<td>23.5</td>
</tr>
<tr>
<td>3-Mercapto-3-methylbutyl formate</td>
<td>77</td>
<td>0.0035</td>
<td>22</td>
</tr>
<tr>
<td>2-Methyl-3-furanthiol</td>
<td>68</td>
<td>0.007</td>
<td>9.7</td>
</tr>
<tr>
<td>Dimethyltrisulfide</td>
<td>28</td>
<td>0.01</td>
<td>2.8</td>
</tr>
<tr>
<td>Methional</td>
<td>228</td>
<td>0.2</td>
<td>1.1</td>
</tr>
<tr>
<td>(E)-β-Damascenone</td>
<td>222</td>
<td>0.00075</td>
<td>296</td>
</tr>
<tr>
<td>Homofuraneol</td>
<td>16800</td>
<td>1.15</td>
<td>14.6</td>
</tr>
<tr>
<td>Furaneol</td>
<td>112000</td>
<td>10</td>
<td>11.2</td>
</tr>
<tr>
<td>Diacetyl</td>
<td>48400</td>
<td>15</td>
<td>3.2</td>
</tr>
<tr>
<td>2,3-Pentanedione</td>
<td>34000</td>
<td>30</td>
<td>1.1</td>
</tr>
</tbody>
</table>

(Grosch et al.)
### Key odorants found in Arabica coffee brew (2)

<table>
<thead>
<tr>
<th>Flavor compound</th>
<th>Concentration (µg/kg)</th>
<th>Odor threshold (µg/kg water)</th>
<th>OAV ($x10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Isobutyl-2-methoxypyrazine</td>
<td>59</td>
<td>0.005</td>
<td>11.8</td>
</tr>
<tr>
<td>2-Ethyl-3,5-dimethylpyrazine</td>
<td>249</td>
<td>0.16</td>
<td>1.6</td>
</tr>
<tr>
<td>2,3-Diethyl-5-methylpyrazine</td>
<td>73</td>
<td>0.09</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Vinylguaiacol</td>
<td>55200</td>
<td>20</td>
<td>2.8</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>3050</td>
<td>2.5</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methylbutanal</td>
<td>18600</td>
<td>0.4</td>
<td>46.5</td>
</tr>
<tr>
<td>Methylpropanal</td>
<td>32300</td>
<td>0.7</td>
<td>46.1</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>139000</td>
<td>10</td>
<td>13.9</td>
</tr>
<tr>
<td>2-Methylbutanal</td>
<td>20700</td>
<td>1.9</td>
<td>10.9</td>
</tr>
<tr>
<td>Propanal</td>
<td>17400</td>
<td>10</td>
<td>1.7</td>
</tr>
</tbody>
</table>

(Grosch et al.)
Sensory profiling of Arabica brew aroma

Similarity: 2.3

(Czerny et al., 1999)
Effect of the base used for sensory profiling (Czerny et al., 1999)

Similarity:  

- Coffee: 3.0
- Cellulose: 1.8
- Oil: 1.6
- Water: 1.0
Effect of odorants on Arabica coffee brew aroma

(Grosch et al., 1998)

Samples

S2
S4
S6
S8
S10
S12

No phenols (4)
No guaiacol
No 4-vinylguaiacol
No 2-furfurylthiol
No pyrazines (4)
No 2-methyl-3-furanthiol
No methanethiol
No methional
No aldehydes (3)
No diones (2)
No 3(2H)-furanones (2)
No (E)-β-damascenone

Positive answers

(Grosch et al., 1998)
## Off-flavor in food products

<table>
<thead>
<tr>
<th>Food</th>
<th>Contamination Prepared meat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Food-born Meat, coffee, spinach</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Odorants</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sensory properties</td>
</tr>
<tr>
<td></td>
<td>Formation pathways</td>
</tr>
<tr>
<td></td>
<td>Decomposition</td>
</tr>
</tbody>
</table>
Off-flavors caused by sulfur compounds

**Meat**

$\text{Meat} \xrightarrow{\text{H}_2\text{S}} \text{SHCO}_2\text{H}

(Patterson, 1969)

**Beer**

$\text{Meat} \xrightarrow{\text{SHCO}_2\text{H}} \text{SH}_2\text{CO}_2\text{H}

(Kuroiwa & Hashimoto, 1961)

(Schieberle, 1991)

**Milk**

$\text{S-CONH}_2 \xrightarrow{\Delta T} \text{SHCO}_2\text{H}

(Masanetz et al., 1998)

**Spinach**

$\text{CN} \text{CONH}_2 \xrightarrow{\Delta T} \text{SHCO}_2\text{H} + \text{SHCONH}_2$

(Masanetz et al., 1998)
Major reactions leading to off-flavor in food

Addition of $H_2S$

- To double bonds
- To $\alpha,\beta$-unsaturated aldehydes

Thermal degradation

- Methionine
- Cysteine

![Chemical structures and reactions](attachment:image.png)
Fish-like off-flavor in dried spinach

(Z)-1,5-Octadien-3-one
Metallic, geranium-like
O\textsubscript{x} = 0.001 µg/L water

Methional
Cooked potato-like
O\textsubscript{x} = 0.2 µg/L water

(Z)-3-Hexenal
Green leaf-like
O\textsubscript{x} = 0.25 µg/L water

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methional</td>
<td>(10 µg/L)</td>
<td>x</td>
</tr>
<tr>
<td>Octadienone</td>
<td>(0.16 µg/L)</td>
<td>x</td>
</tr>
<tr>
<td>(Z)-3-Hexenal</td>
<td>(4.3 µg/L)</td>
<td>-</td>
</tr>
</tbody>
</table>

Fishy (2), green (0.5)
Potato (1), metallic (1.5)

Fishy (1.5), green (2)
Potato (1), metallic (1.5)

(Masanetz et al., 1998)