

ADVANCED BEER AROMA ANALYSIS

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Beer Analysis - Overview

- Production of Beer
- Sample Preparation and Analysis
- Relevance of Aroma Fingerprinting
- Comprehensive GCxGC-MS
- Targeted Analysis of Flavor and Off Flavour Compounds-Enhancing Selectivity and Sensitivity

Production of Beer and Aroma Influencing Steps

Maillard reaction products



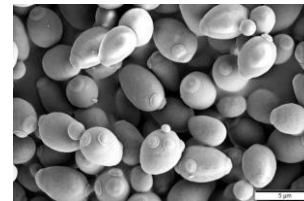
Malt

~ 30 odor active compounds contribute to the aroma



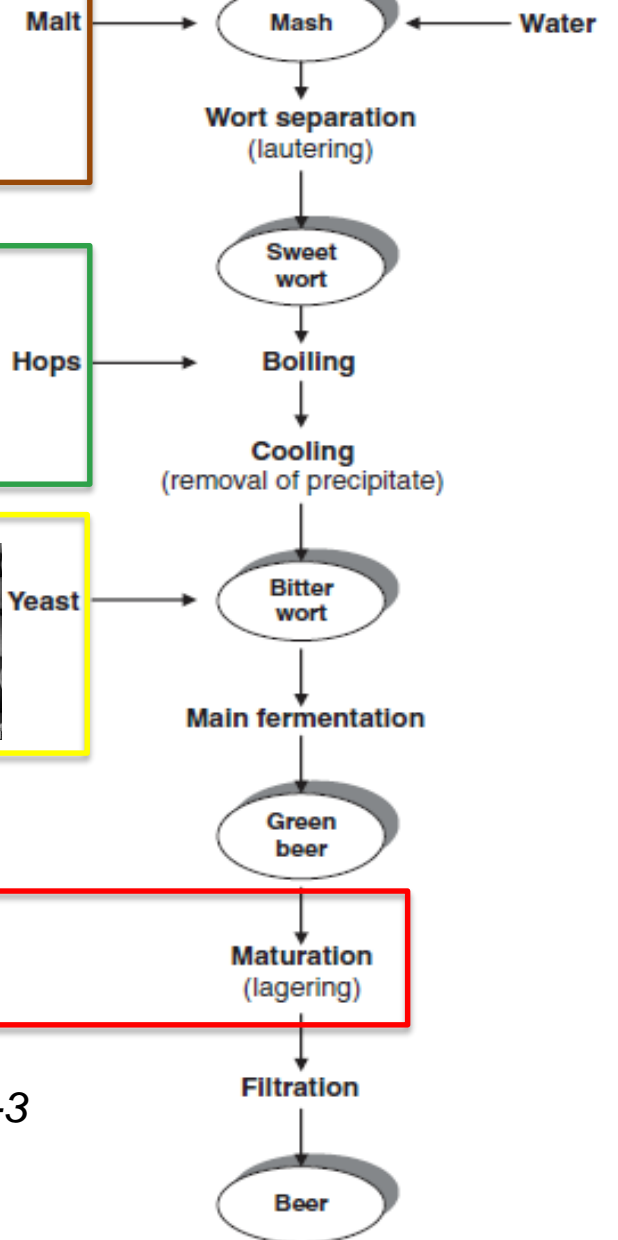
Hops

Massive influence due to yeast activity
Mainly formation of alcohols and esters...



Yeast

Ageing flavours (light, temperature, oxygen...)



L.C. Verhagen, *Beer Flavour* <https://doi.org/10.1016/B978-008045382-8.00087-3>

Aroma Compounds in Beer

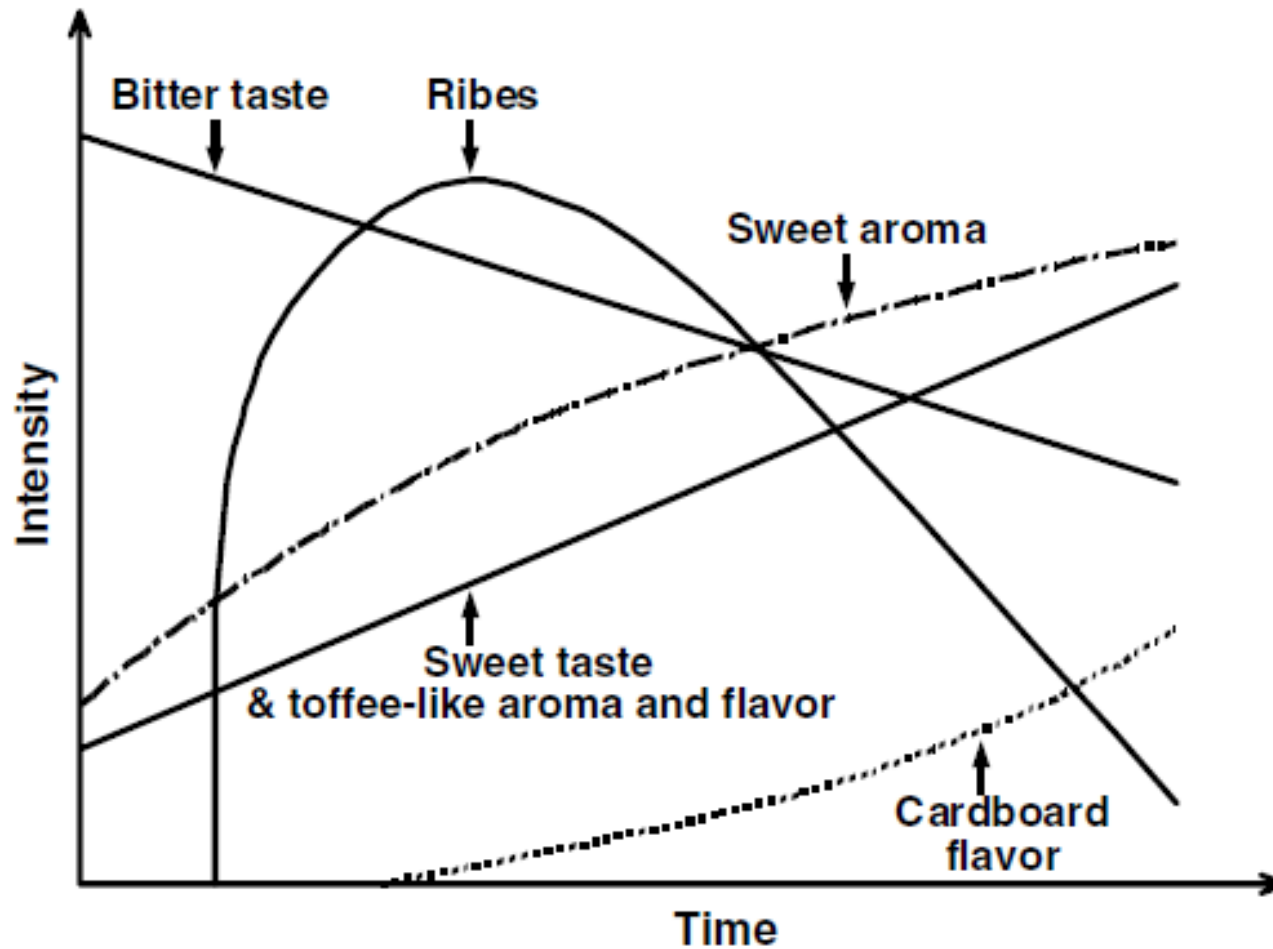
So far several hundred volatiles from different chemical classes are identified in beer

| Compound Class | Substance | Sensory Threshold [$\mu\text{g/L}$] | Odor |
|-------------------|--------------------|--|--------------------------|
| Organic acids | Butanoic acid | 1000 | Sweat, rotten milk |
| Ester | Isoamylacetate | 510 | Banana |
| Higher alcohols | 2-Methylbutanol | 320 | Fusel alcohol |
| Vicinal diketones | Diacetyl | 17 | fermented milk |
| Guaiacols | Guaiacol | 2.5 | medicinal, smoky |
| Terpenes | (R)-Linalool | 0.14 | Earl Grey Tea, citrus |
| Aldehydes | E-2-Nonenal | 0.03 | Cardboard |
| Sulfur compounds | Dimethyltrisulfide | 0.03 | Onion, rotten veggies |

D. Saison et al. / Food Chemistry 114 (2009) 1206–1215 1209

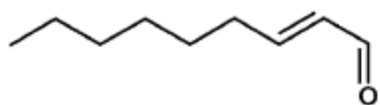
H.T. Fritsch et al. / J. Agric. Food Chem. 2005, 53, 7544-7551

Sensory Changes during Beer Ageing

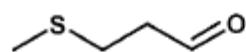


B. Vanderhaegen et al. / Food Chemistry 95 (2006) 357–381

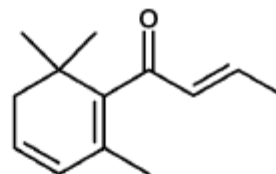
Ageing Flavours



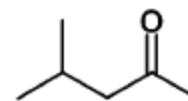
(I)



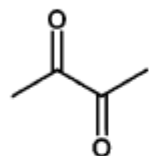
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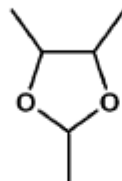
(III)



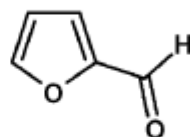
(IV)



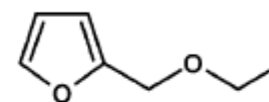
(V)



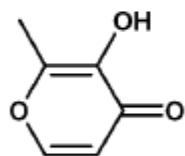
(VI)



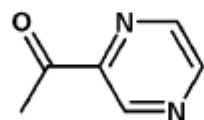
(VII)



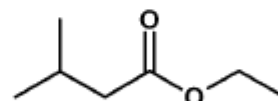
(VIII)



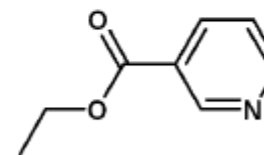
(IX)



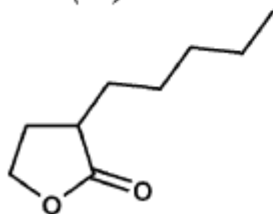
(X)



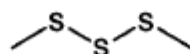
(XI)



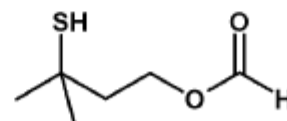
(XII)



(XIII)



(XIV)



(XV)

 Chemical class

Linear aldehydes

Strecker aldehydes

Ketones

Cyclic acetals

Heterocyclic compounds

Ethyl esters

Lactones

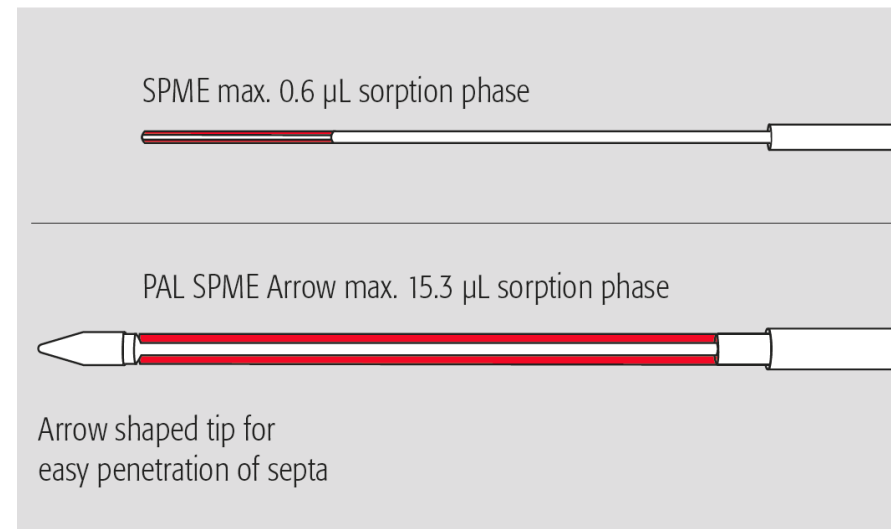
S-compounds

B. Vanderhaegen et al. / Food Chemistry 95 (2006) 357–381

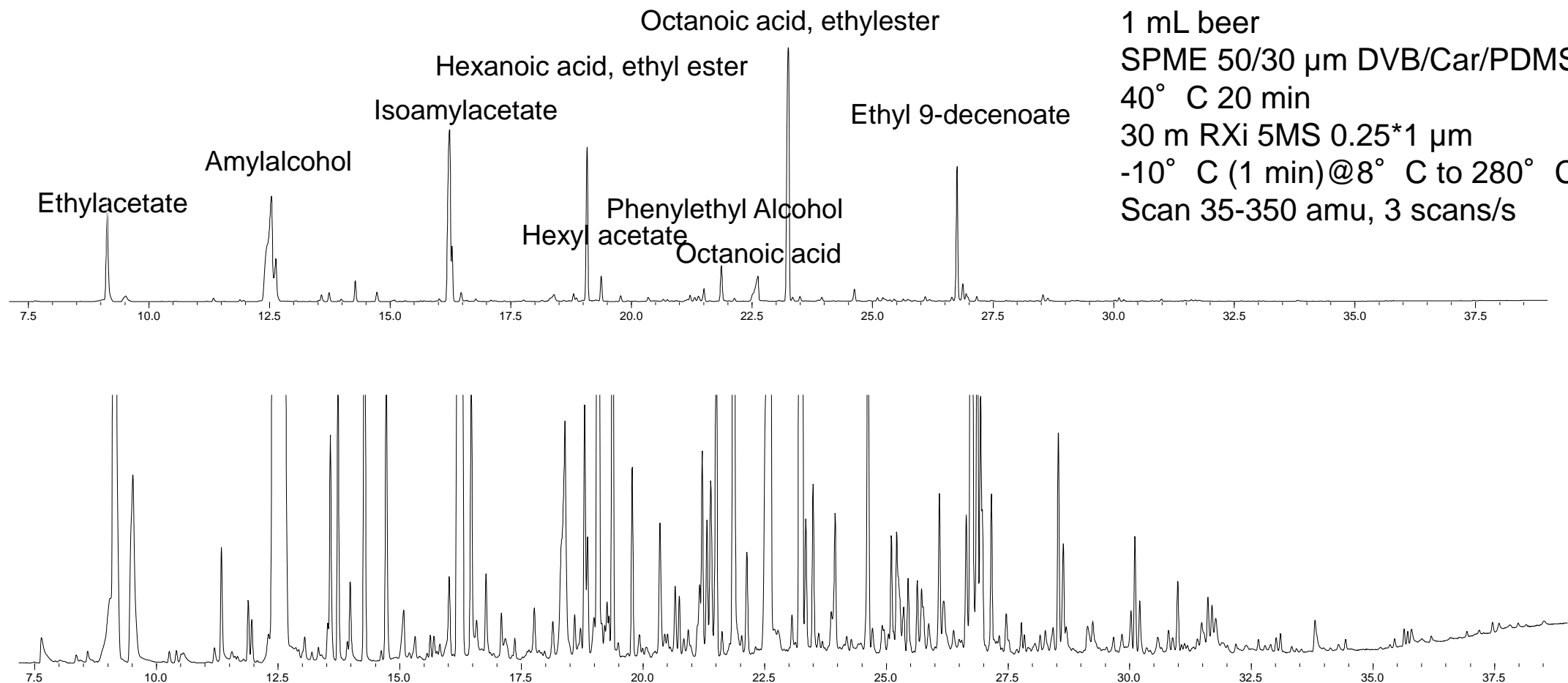
Sample Preparation based on SPME



NO solvent, NO waste
NO non volatiles
NO cross contamination from the solvent
Fast and simple
High throughput using autosampler
Typical sample size 0.1-2 mL
SENSITIVE ~ 1 μ g/L in full scan

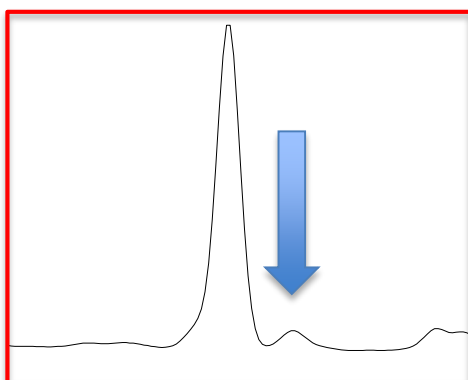
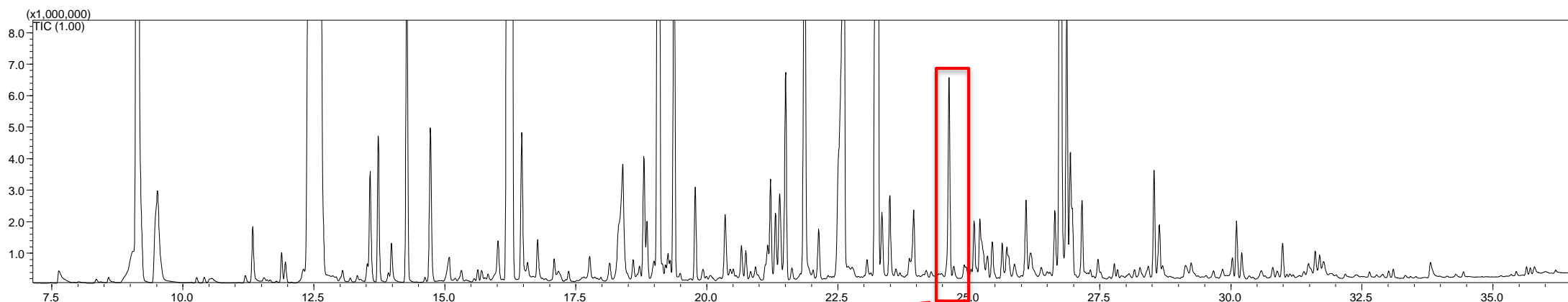


Special Shimadzu RAFA Beer



Bottom fermented Pils lager beer brewed by Prof. Pavel Dostalek from the University of Chemistry and Technology, Prague especially for RAFA

Automated Retention Index Calculation and Identification

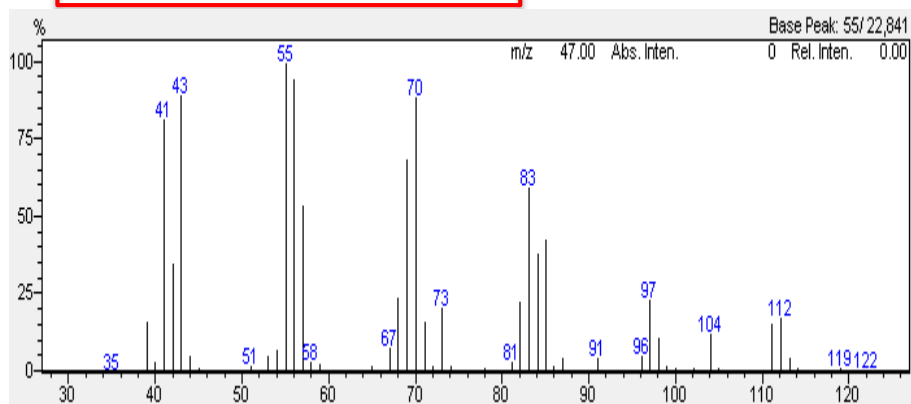


Automated RI calculation

| ID# | Name | Ret. Time | Ret. Index |
|-----|----------------------|-----------|------------|
| 47 | 2-Nonanol, acetate | 23.950 | 1233 |
| 48 | Acetic acid, 2-pheny | 24.625 | 1269 |
| 49 | 1-Decanol | 24.715 | 1274 |
| 50 | 3-Nonenoic acid, et | 24.915 | 1284 |
| 51 | Nonanoate <ethyl-> | 25.105 | 1294 |

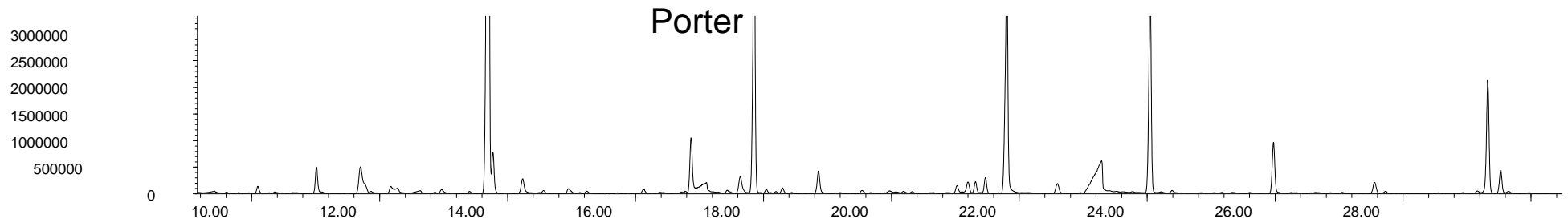
MS Database search

| Hit | Simil | Ret. | Compound Name | Mol Wt | Formula | Library |
|-----|-------|------|---|--------|---------|-------------|
| 1 | 93 | 1258 | 1-Decanol \$\$ Decyl alcohol \$\$ n-Decan-1-ol \$ | 158 | C10H22O | NIST14s.lib |
| 2 | 92 | 1278 | Decyl alcohol \$\$ 1-Decanol | 158 | C10H22O | FFNSC 3.lib |
| 3 | 91 | 1258 | 1-Decanol \$\$ Decyl alcohol \$\$ n-Decan-1-ol \$ | 158 | C10H22O | NIST14s.lib |

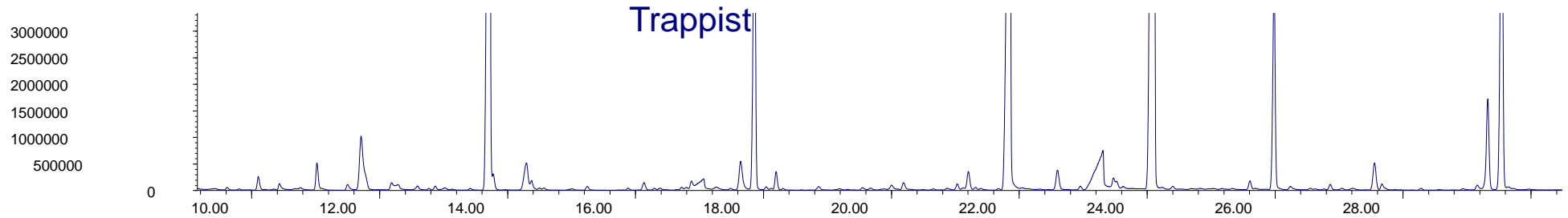


Aromaprofiles

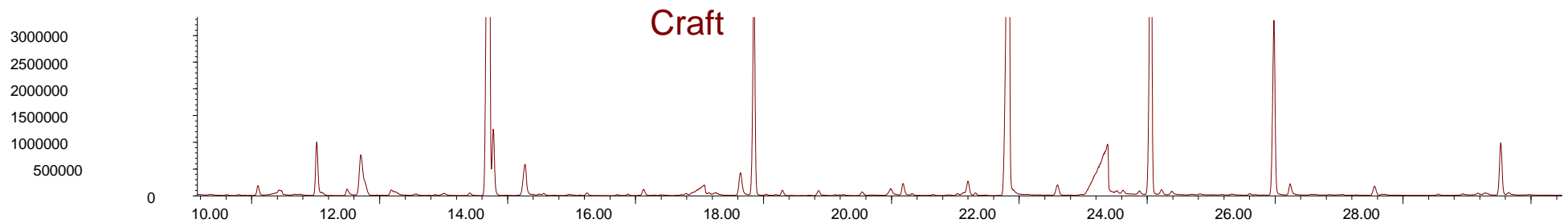
Abundance



Time-->
Abundance

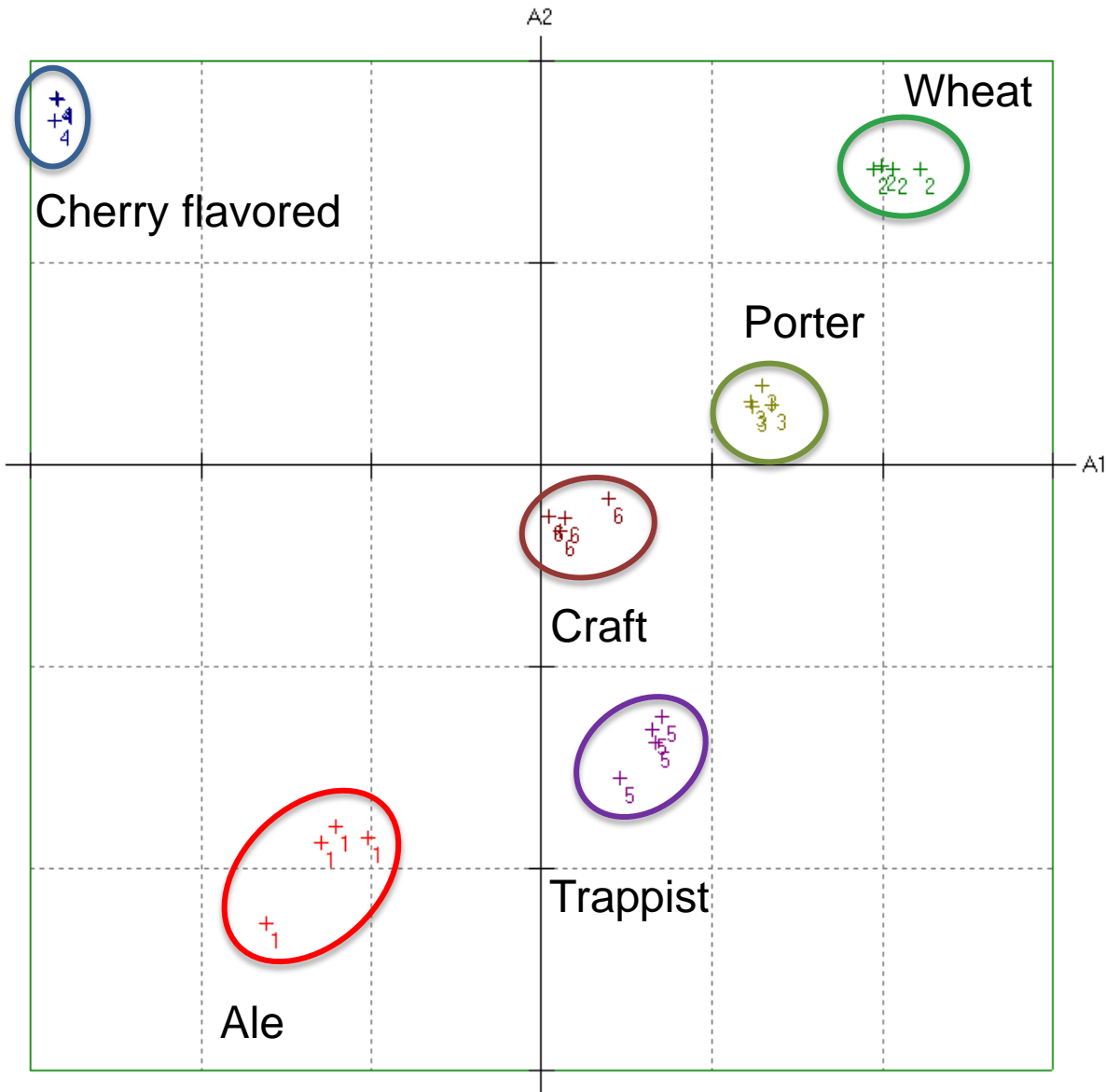


Time-->
Abundance



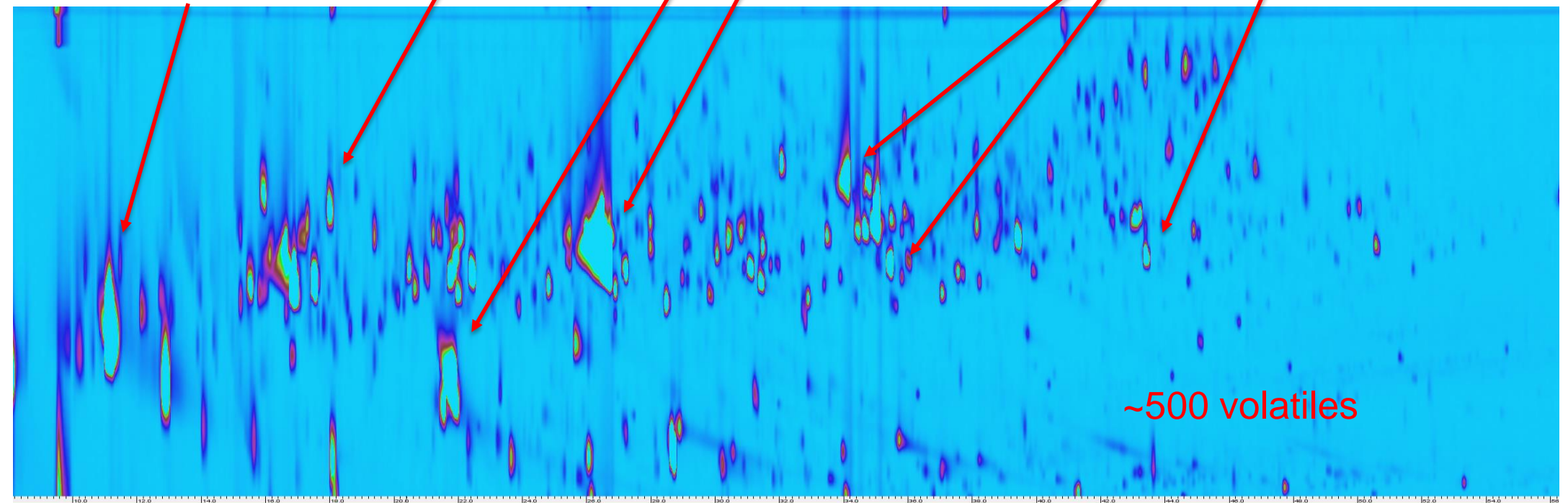
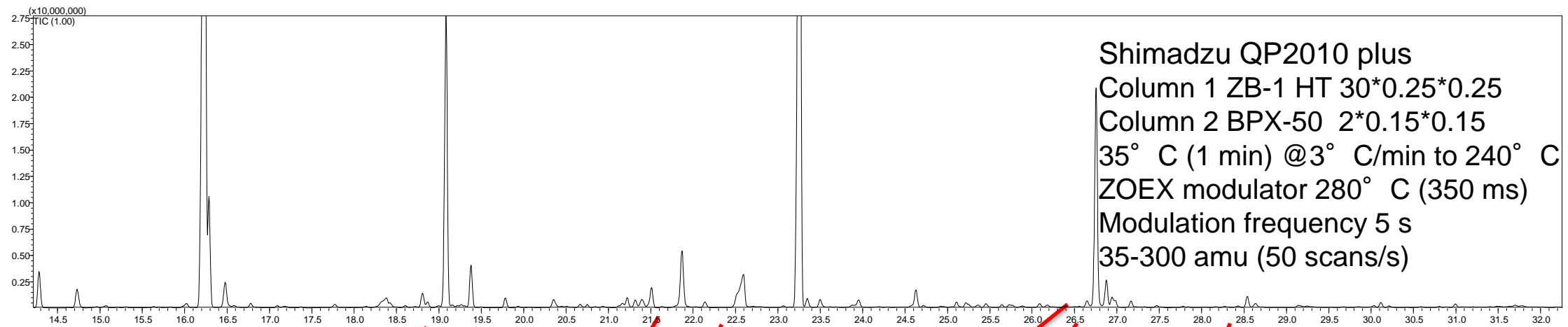
Time-->

Statistical Analysis



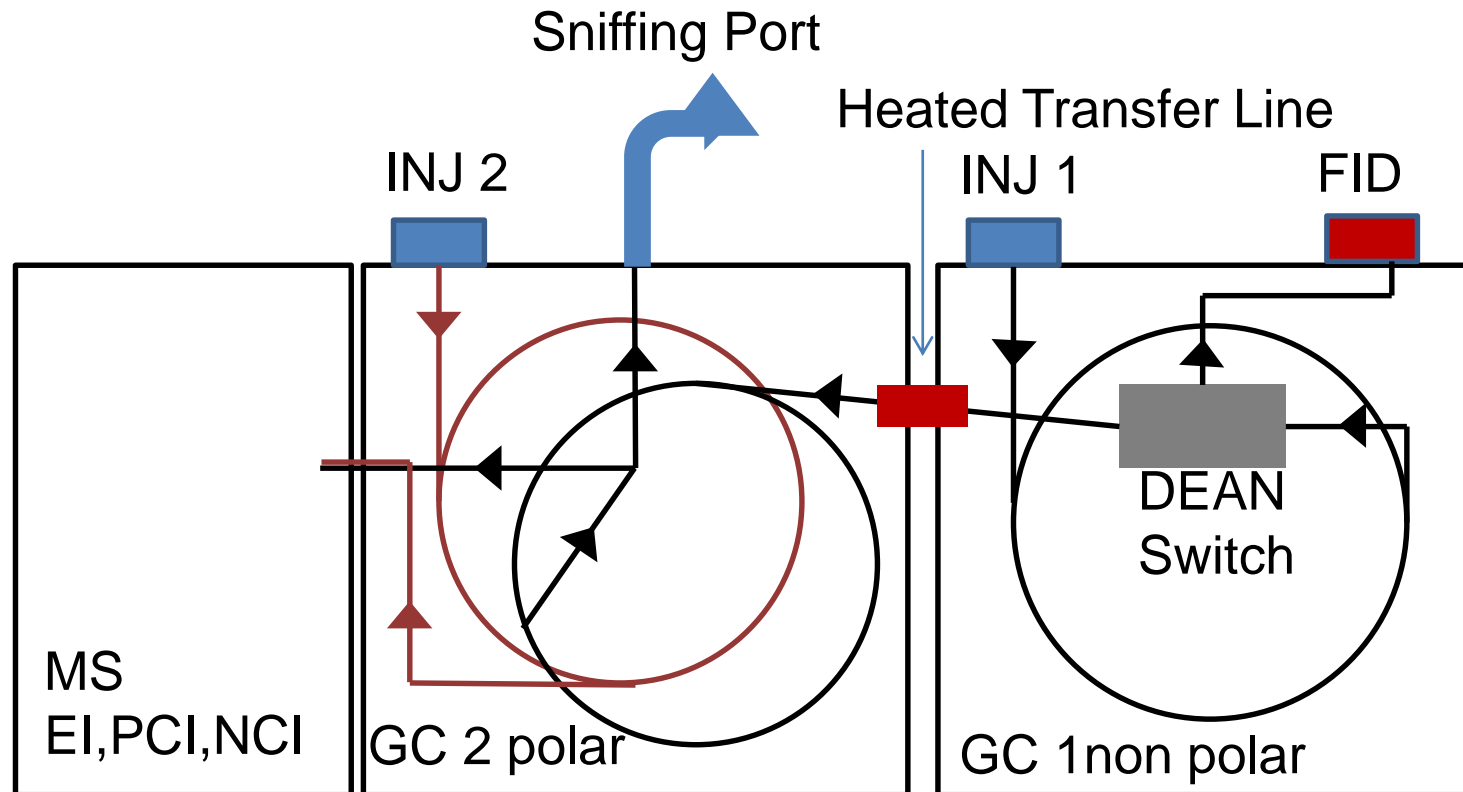
Statistical Analysis can be helpful in the differentiation of different beer varieties

Comprehensive GCxGC-MS



Targeted Analysis of Flavor and Off Flavour Compounds-Enhancing Selectivity and Sensitivity

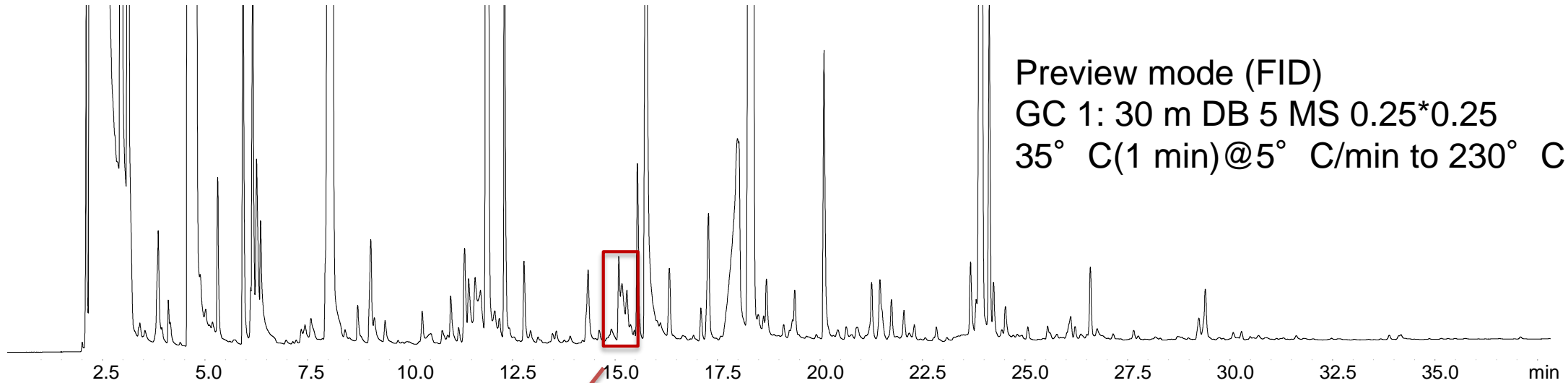
Enhancing Separation-MD GC



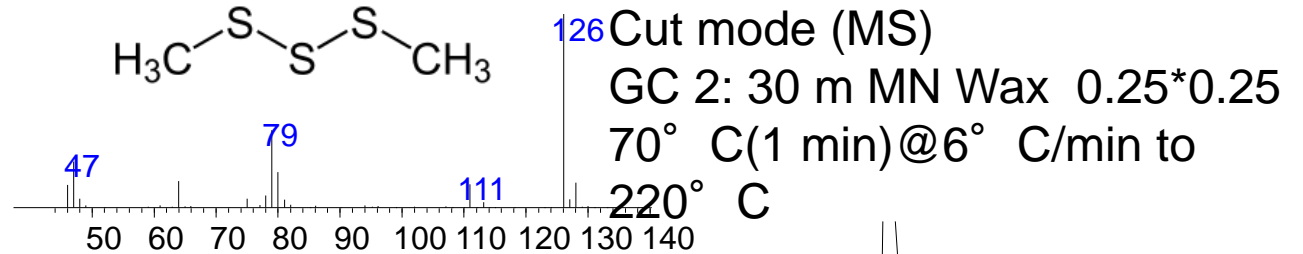
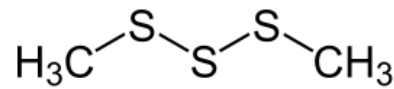
Switching Program :

| | | From | To | |
|---|-------------------------------------|-------|-------|---|
| 1 | <input checked="" type="checkbox"/> | 7.03 | 7.25 | ▲ |
| 2 | <input checked="" type="checkbox"/> | 8.85 | 9.09 | |
| 3 | <input checked="" type="checkbox"/> | 10.64 | 10.89 | ▼ |

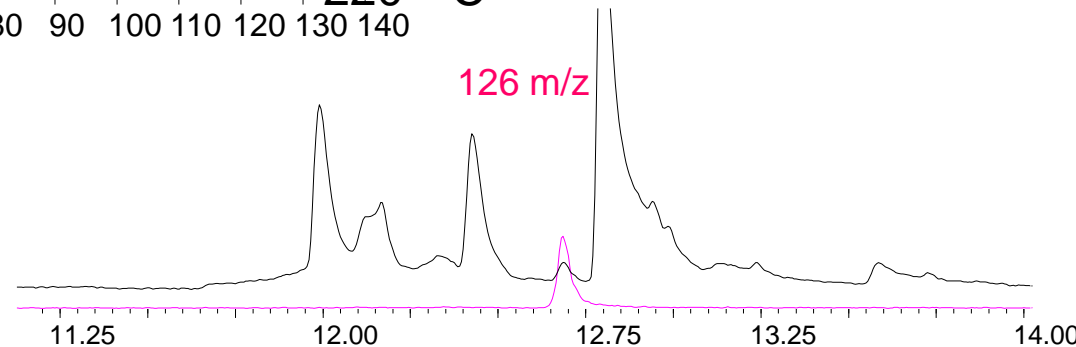
MDGC Determination of Dimethyltrisulfide (DMTS)



30 s
transfer to column 2

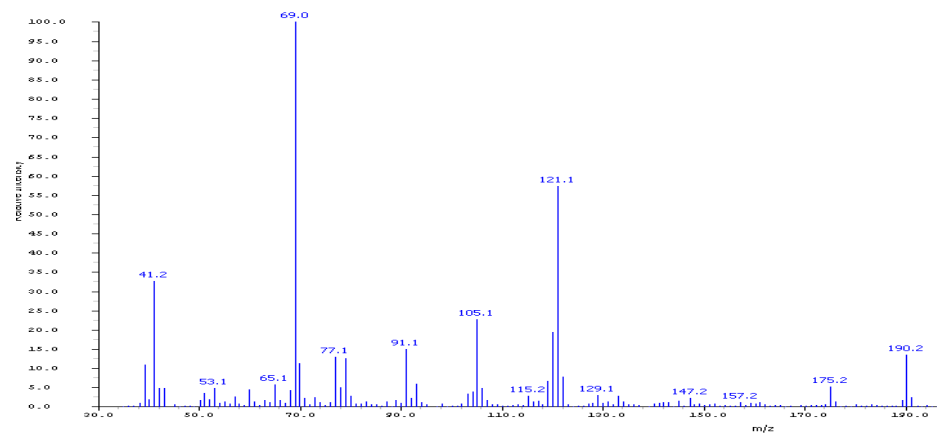
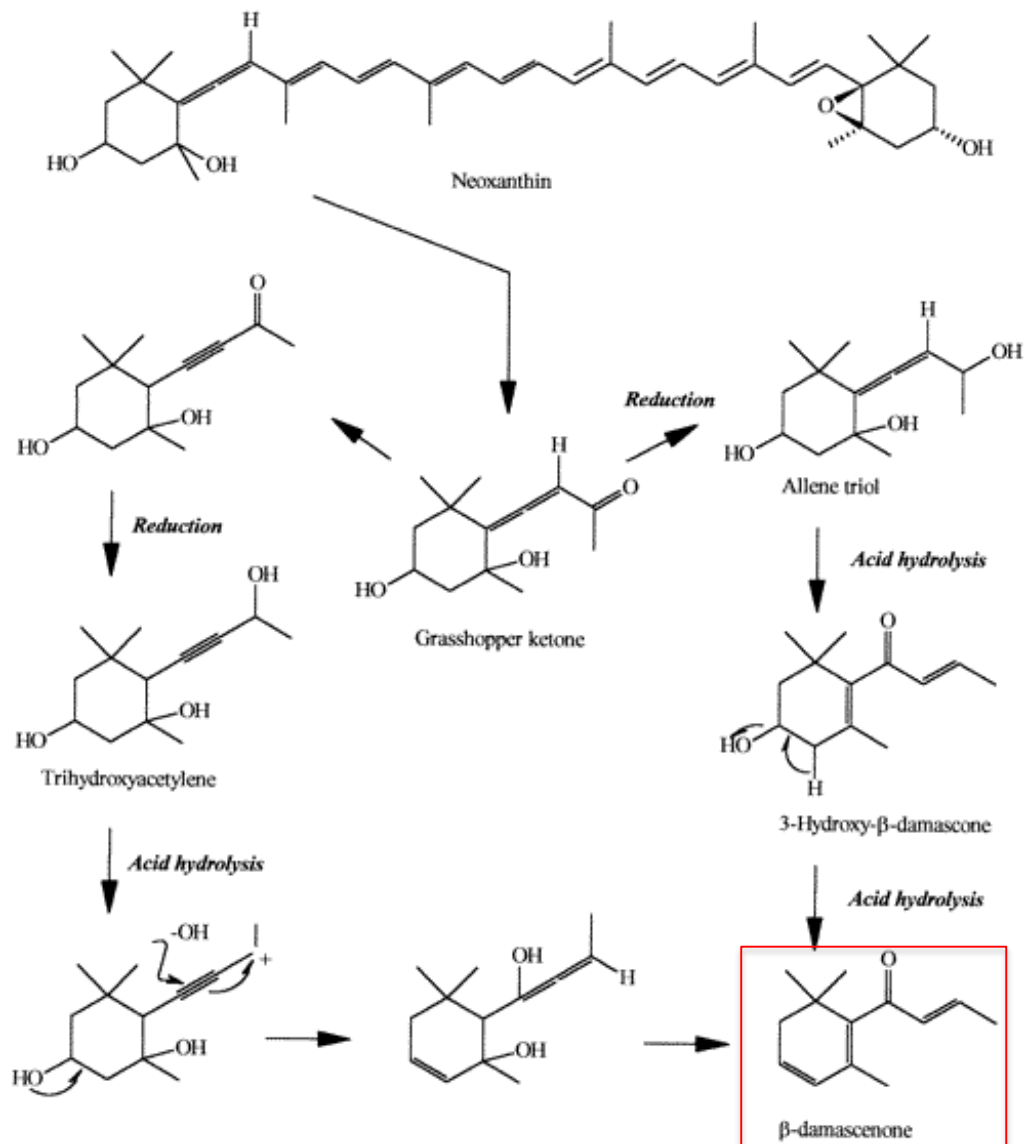


126 m/z



Enhancing Selectivity – Tandem MS

Determination of β -Damascenone



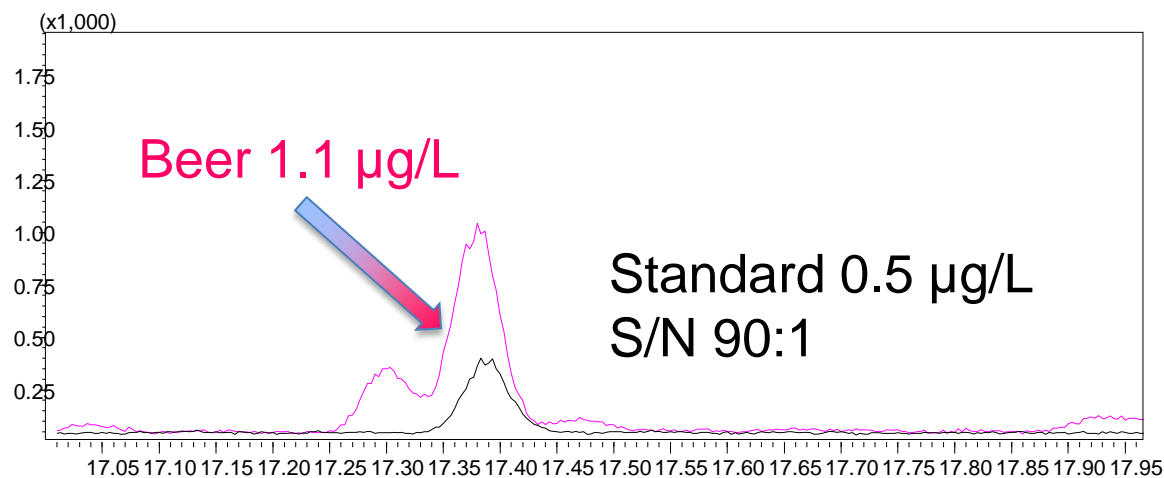
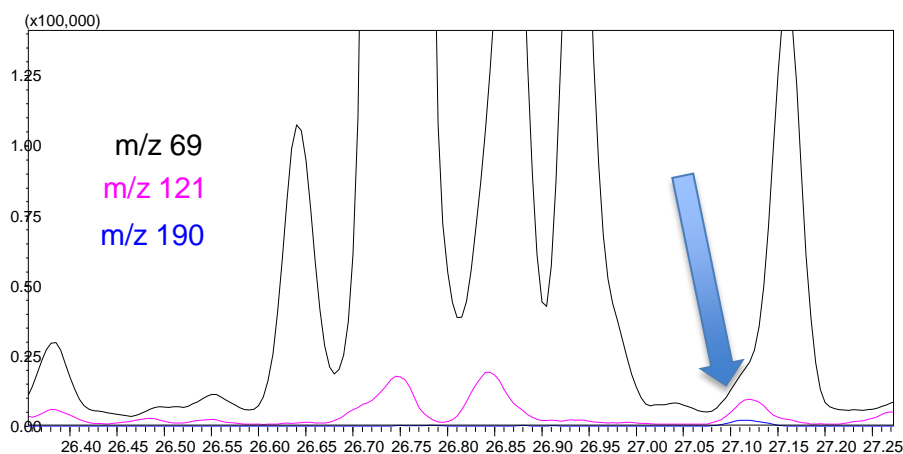
(E)- β -damascenone belongs to a class of carotenoid-derived carbonyl compounds. It is formed by degradation of neoxanthin, which is present in the basic ingredients of beer

Sensory threshold
0.02-0.09 $\mu\text{g/L}$

Odor descriptor
fruity, cooked apples, coconut, tobacco, red

F. Chevance et al./J.Agric.Food Chem. 2002, 50, 3818-3821

Scan vs MS-MS



Sample size 2 mL

Interferences with coeluting compound

Scan 35-300 amu

5 scans/s

RXi5MS 30 m*0.25*1 µm

-10° C(1 min)@8° C/min to 280° C

Sample size 0.1 mL

No interferences

Transitions 121>105 CE 10

121>77 CE 25

5 scans/s

ZB5MS 30 m*0.25*0.25 µm

40° C(1 min)@10° C/min to 100° C

@ 4° C/min to 160° C

@25° C/min to 280° C



Thank you for your attention...
and enjoy the special Shimadzu RAFA beer