

# PROCESS CONTROL FOR H<sub>2</sub>S & THIOL LEVELS IN BEER: GAUGE

## Gauge:Sensory

**Flavor Thresholds:** 0.1, 5-8, 7.5, 20 & 20 for DMTS, H<sub>2</sub>S, DMDS, MTA and DMS, respectively.

**Aromatraz:** sulfur notes include.....sulfury, cooked vegetable, sauerkraut, skunky, cheesy, onion, garlic, rubber, burnt rubber, smoky. **Cooked vegetable** linked to **methanethiol**.

Flavor thresholds: DMDS (3-50 ppb), methylthioacetate (300 ppb), methanethiol (3 ppb) & ethanethiol (0.6 ppb). During sample preparation, methanethiol can convert to DMDS & DMTS!

**Miller:** report three cmpds imparting "skunky" sensory notes detected by GCO:  
i) 3-MBT  
ii) methyl-(3-methyl-2-butene) disulphide,  
iii) methyl-(3-methyl-2-butene) trisulphide,  
.....retention times of 9.94, 17.98 and 23.33 minutes, respectively, using "**multidimensional heart-cutting technique**" to isolate interference from "non-odorous" compounds.

"**Sensory synergism**".....sulfur off-flavors resulting from shifts upwards in [thiols] even though each still < threshold.

**Sensory threshold for 3-MBT is @ 1.3-4.4 ppt.**

H<sub>2</sub>S **flavor threshold** is 3-10 ppb.

Methional: "boiled potato"  
Methionol: "soup".

## Gauge:Sensory

DMTS...flavor threshold in beer of 0.1 ppb ....onion-like off-flavor...Belgians feel it is formed from the reduction of malt derived 3-methylthiopropionaldehyde during aging...linear relationship between malt color and levels of MTP in wort...levels of Cu, Fe, SO<sub>2</sub>, ascorbic acid or riboflavin could drive production of DMTS during aging either up or down.

**Strecker aldehydes:** **US lager** beer spiked with **methionine** develop higher levels of **methional and sulfury flavors**....same thing done with **European lagers results in stale "cardboard"** from formation of aldehydes by Strecker degradation, not sulfury flavors. European pattern also seen if spike with valine, leucine or phenylalanine).

**GC/O studies using Supelco "Amberlite XAD-2"** resin revealed the presence of the following thiols in fresh beer: **3MBT**, **3MH** (3-mercaptohexan-1-ol) and **4MMP** (4-mercapto-4-methyl-pentan-2-one). **Adding copper to beer decreased the volatility of these thiols, thereby increasing their flavor threshold and making them less perceptible!!**

H<sub>2</sub>S reacts easily with organic compounds to form highly flavor active by-products.

Residual H<sub>2</sub>S in beer smells sulfury and harsh and is the typical character of green beer.

Static headspace injection cannot provide accurate R&R for many ppb/ppt sulfur compounds - pre-[ ] needed e.g. purge & trap SPME.

## Gauge:Chemistry

## Gauge:Chemistry

Extraction of thiols from beer: trapping thiols with p-hydroxymercuribenzoic acid, then analysis of extracts by GC/MS, GCO and GC/PFPD (pulsed flamephotometric detection). Identified 11 thiols in 4 lagers:  
i) 3-mercaptohexanol ("rhubarb" flavor)  
ii) 4-mercapto-4-methyl-2-pentanone ("Blackberry" or "box tree")  
iii) 3-mercaptopropyl acetate ("roasted meat")  
iv) 2-mercapto-3-methylbutanol ("onions" or other vegetables.  
v) 2-mercaptoethyl acetate ("toasted" or "empyreumatic").  
vi) 3-MBT also detected – even without light exposure!

**SPME** compounds by GC-SCD: DMS, methanethiol, DMDS, MTA, H<sub>2</sub>S (early).

Strecker aldehydes derived from methionine, s-methylcysteine.

## Sulfidic Levels in Beer

Cadmium-sulfide-methylene blue assay.

**Silver nitrate** strips over 0.001 to 50 ppm range..

Thiol Compound/MOA/CV/Detection Limit:  
i) H<sub>2</sub>S/PMS/4.1-5.7%/0.4 ppb  
ii) MT/Purge & trap/87%/0.17 ppb  
iii) DMTS/P&T/1.1%/0.60 ppb  
iv) MTac/SPME/8.7-10.4%/not given.

**CB survey:** SPME of many ales/lagers shows **DMS** and **MeSH** exceed flavor thresholds.

[H<sub>2</sub>S] as reacts with organics to form complex sulfur compounds (+) ....CB does not agree.

Purge & Trap

GC/SCD: Used for MTA, DMDS, methanethiol

**SPE = Solid Phase Extraction.**

Copper is claimed to catalyze H<sub>2</sub>S formation.....also Cu + H<sub>2</sub>S yields CuS.

**Lead acetate** impregnated sticks for qualitative assessments.

**SIDA: Stable Isotope Dilution Assay**

Reaction with stainless steel injection needles/surfaces can reduce [sulfur] compounds actually entering GC columns.

**Amperometric Sulfur Detection (ASD)** exceeds SCD for detecting sulfur compounds such as H<sub>2</sub>S.

**GC** methods of analysis very poor R & R..."DT" method (**D**etection **T**ube) much more accurate and direct.

**ASBC No. XVIII**  
(Casey;  
May/06)