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Rapid quantification of major hop aroma compounds in beer by static headspace GC-MS

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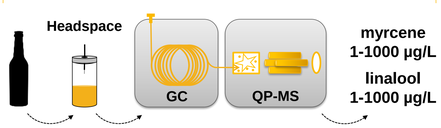
Abstract

5 samples per hour



Hop aroma in beer, it's complicated…

- Hop aroma is a primary quality characteristic of many beer styles.
- Numerous techniques for quantification of hop aroma compounds in beer have been published, the vast majority is GC-MS based.
- There is no short and universal list of relevant hop aroma compounds. Analysts use custom made target lists, typically including 20 (or more) analytes. In order to maximize the number of target compounds, selective extraction techniques such as Solid Phase Microextraction (SPME) or Stir Bar Sorptive Extraction (SBSE) and long GC runtimes are applied.
- All in all, hop aroma analysis appears to be a rather complex and costly discipline.

Respecting the needs for fast, simple, and cost effective assays, the current poster introduces a rapid static headspace-GC-MS method for quantification of the relevant hop components myrcene and linalool by a stable isotope dilution assay.

Method

Sample preparation

- 2 mL beer + 1 g NaCl + 20 µL internal standard (d_2-myrcene/d_5-linalool [0.01 mg/mL]) were added into a 10 mL headspace vial with a magnetic screw cap.

Incubation: 65 °C, 500 rpm,10 min
Sampling: 1 mL headspace syringe at 70 °C
Injection: Split injection 1/15 at 250 °C

GC-MS parameters

- Separation on HP-5MS UI (30 m x0.25 mm x0.25 µm)
- Temperature program:
  80 °C (1 min)
  5 °C/min to 110 °C
  50 °C/min to 300 °C (1 min)
  run time = 11.8 min
- EI-SIM-MS

myrcene	*m/z*= 93.3 + 121.3
d_2-myrcene	*m/z*= 95.3 + 123.3
linalool	*m/z*= 71.3 + 93.4
d_5-linalool	*m/z*= 74.4 + 98.4

Method validation

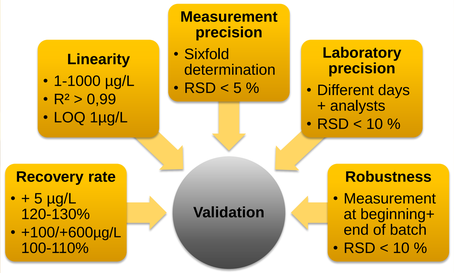


Figure 1: Parameters and results of method validation.

Results and discussion

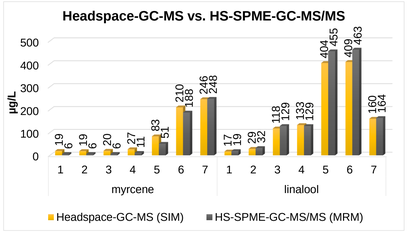


Figure 2: Comparison of the new rapid headspace-GC-MS method with reference method with 7 different beers. The samples are measured in duplicates (RSD < 10%).

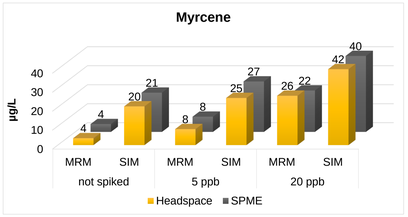


Figure 3: Determination of recovery rate by measuring headspace/ SPME method both in SIM and MRM mode. A Pilsen beer was spiked.

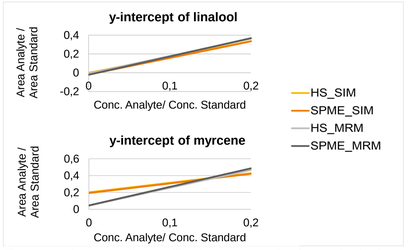


Figure 4: Corresponding calibration curves (in beer simulant) to measurements of Fig. 3. Comparison of y-intercept of myrcene and linalool.

Experiment 1

In addition to method validation (Fig. 1) a comparative study using HS-SPME-GC-MS/MS as reference method (Fig. 2) was carried out. For SPME a DVB/CAR/PDMS fiber was used (extraction: 5 min; desorption 60 s).
Validation showed:

- ✓ Linalool RSD < 10 % in all samples tested
- x Myrcene RSD ranged from 75% to < 10% depending on myrcene level

Are deviations in myrcene concentrations caused by different enrichment techniques (HS/ HS-SPME) or by different measuring methods (SIM/ MRM)?

Experiment 2

Applying all possible combinations of sample preparation and detection (HS/ HS-SPME and SIM/ MRM) showed (Fig. 3):

- Individual myrcene recovery rate for each measurement method are considered good (85-130%).
- Deviation of the myrcene concentration is caused by MRM/ SIM measurement mode, not due to different enrichment techniques.
- With increasing concentration, the myrcene values measured by MRM/ SIM approximate (Figs. 2 and 3).

In order to understand why the myrcene concentrations determined in the MRM mode are lower, it is helpful to have a closer look on the calibrations graphs (Fig. 4).

- Calibration curves (SIM vs. MRM) for linalool match
- SIM calibration curve for myrcene shows a higher Y-axis-intercept than the corresponding MRM curve.

Explanation: In the SIM mode, one or several matrix constituents exhibiting ions with m/z 93.3 coelute with myrcene. Those are eliminated by selective MRM transition (m/z 93.3 → m/z 77).

Conclusion

- A fast, simple, and cost effective headspace-GC-MS method for quantification of myrcene and linalool has been successfully developed.
- By focusing on two major hop aroma compounds GC runtime is short and costly SPME sampling does not add any benefit.
- Results of HS-GC-MS and HS-SPME-GC-MS/MS match, deviations at low myrcene concentrations trace back to co-elutions in GC.
- When analyzing hoppy beers both, SIM or MRM mode, are applicable.
- In summary the method is, as intended, useful for fast estimations of major hop aroma compounds in beer.

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