

Determination of Vicinal Diketones in Beer

Headspace GC-IMS Analysis



Introduction

Diacetyl, or 2,3-butanedione, is a flavour component that naturally occurs in several foods. It provides the buttery smell of butter and popcorn.

Since diacetyl is a by-product of fermentation processes by yeast this buttery aroma can result in an undesirable *off-smell* for some products. A well known example is the diacetyl generation during the beer brewing process



Figure 1: FlavourSpec®

Yeast metabolizes the diacetyl it produced before. Since this *diacetyl residual* is a time- and energy- consuming process a frequent determination of the diacetyl concentration is necessary. FlavourSpec® detects the vicinale diketones diacetyl and pentanedione directly in the headspace of beer samples. By that the workflow is reduced to sampling, analysis runtime and automated quantification based on calibration data.

Experimental

All measurements were carried out with the FlavourSpec®, a GC-IMS equipped with an autosampler with headspace option. For the efficient separation an isothermal heated capillary column is used (5% diphenyl - 95% dimethyl polysiloxane, 60 m x 0.32 μm x 1 μm). To ionise the molecules a ^3H source is used. The activity with 300 MBq is below the threshold of 1 GBq so that no licence is required in all EURATOM countries. The measurement parameters are listed in table 1.

In a first step the beer samples have to be degassed to prevent pressure changes in the vial due to the evaporation of CO_2 . This can be done by filtering the beer sample using silica gel or by ultra sonication.

5 mL of the beer sample is filled into a 20 mL headspace vial and sealed with a magnetic cap. The vial is heated in the agitator for a time of 90 min to 65 °C to convert all precursors to diacetyl.

Advantages of G.A.S. mbH FlavourSpec® for routine beer analysis:

- No license for radioactive source required
- No need for Helium
- System operation intuitive and simple to learn
- Easy in use software and report generation
- Very low maintenance costs
- High reproducibility and accuracy

The FlavourSpec® is calibrated using calibration solutions with concentrations of 0.01, 0.025, 0.05, 0.1, 0.2, 0.4 and 0.5 mg/L of diacetyl and pentanedione in 5% ethanolic/water solution.

Data Analysis

The data analysis is done by the easy-to-use software *BeerAnalyser* developed by G.A.S. mbH (figure 2).

Using the *BeerAnalyser* sample names can be transferred to the FlavourSpec® to rename the samples automatically. After the measurement of the calibration solutions the function for both compounds automatically is calculated on the basis of the total ion current of the maximum peaks of diacetyl and pentanedione within a pre-defined area set.

Once the system is calibrated the *BeerAnalyser* is ready to calculate unknown concentrations of diacetyl and pentanedione of the analysed beer samples and to generate the reports with the results by just one “click” (figure 3).

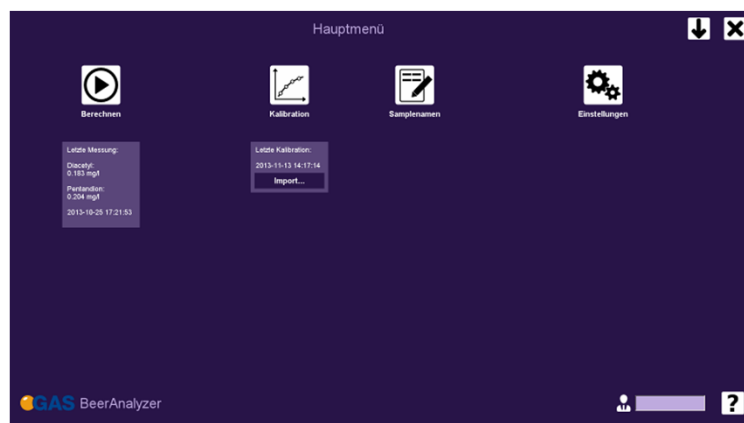


Figure 2: G.A.S. mbH Software *BeerAnalyser*

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Diacetyl/Pentanedione Measurement

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Base Data

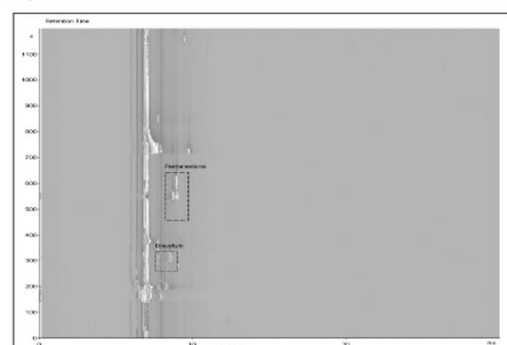
| | |
|-------------------|------------------------|
| Device: | 1H1-00033 |
| Acquisition Date: | 2013-10-28 16:46:22 |
| Measurement File: | 131028_104622_0T05.mea |
| Operator: | |
| Software Version: | BeerAnalyser 1.0.0 |
| Last Calibration: | 2014-01-22 11:39:59 |

Result

| | | |
|----------------|----------------------|--------------------------|
| Concentration: | Diacetyl: 0.056 mg/l | Pentanedione: 0.090 mg/l |
|----------------|----------------------|--------------------------|

Analytical Data

| | | |
|-------------------------------|----------------------|--------------------------|
| Intensity: | Diacetyl: 0.226 V/ms | Pentanedione: 0.457 V/ms |
| Drift Time: | 8.560 ms | 9.020 ms |
| Retention Time: | 305.000 s | 547.000 s |
| Target Area - Drift Time: | 7.660-9.013 ms | 8.201-9.663 ms |
| Target Area - Retention Time: | 263-336 s | 457-543 s |



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Figure 3: Report with results and all relevant parameters generated by G.A.S. mbH *BeerAnalyser*

Table 1: Analysis Conditions

| | | |
|---------------------|---------------------------|------------------------------------|
| FlavourSpec® | | |
| | Polarity IMS | Negative |
| | T1 (IMS) | 60°C |
| | T2 (DB-5, 60m) | 50°C |
| | T3 (Injektor) | 60°C |
| | T4 (Transferline) | 50°C |
| | E1 (Driftgas flow rate) | 150 mL/min Nitrogen 5.0 |
| | E2 (Carriergas flow rate) | 5 mL/min Nitrogen 5.0 |
| | Run time | 20 min |
| | Average | 12 |
| Agitator | | |
| | Incubation temperature | 65 °C |
| | Incubation time | 90 min |

Results

A typical result of a measurement of diacetyl and pentandion in beer is shown in figure 4. The peak position of pentandion is used as marker for the definition of the peak area of diacetyl.

The calibration curves calculated with the *BeerAnalyser* for diacetyl and pentandion are shown in figure 5 in the concentration range of 0.01 mg/L and 0.5 mg/L. The standard deviation is in the range of 5 %.

Results of measurements for beer samples taken from a fermentation tank compared to a standard gas chromatographic system with an ECD detector (ECD = Electronic Capture Detector) are shown in figure 6. The results show the very good correlation between both technologies.

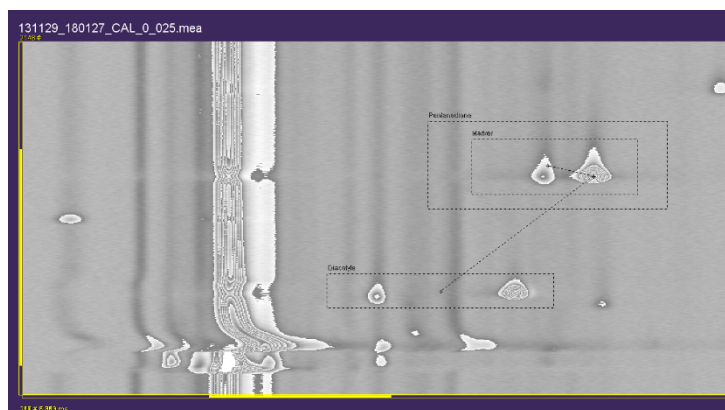


Figure 4: Typical GC-IMS chromatogram of a beer sample



Figure 5: Calibration curves for diacetyl and pentandion (using the *BeerAnalyser*)

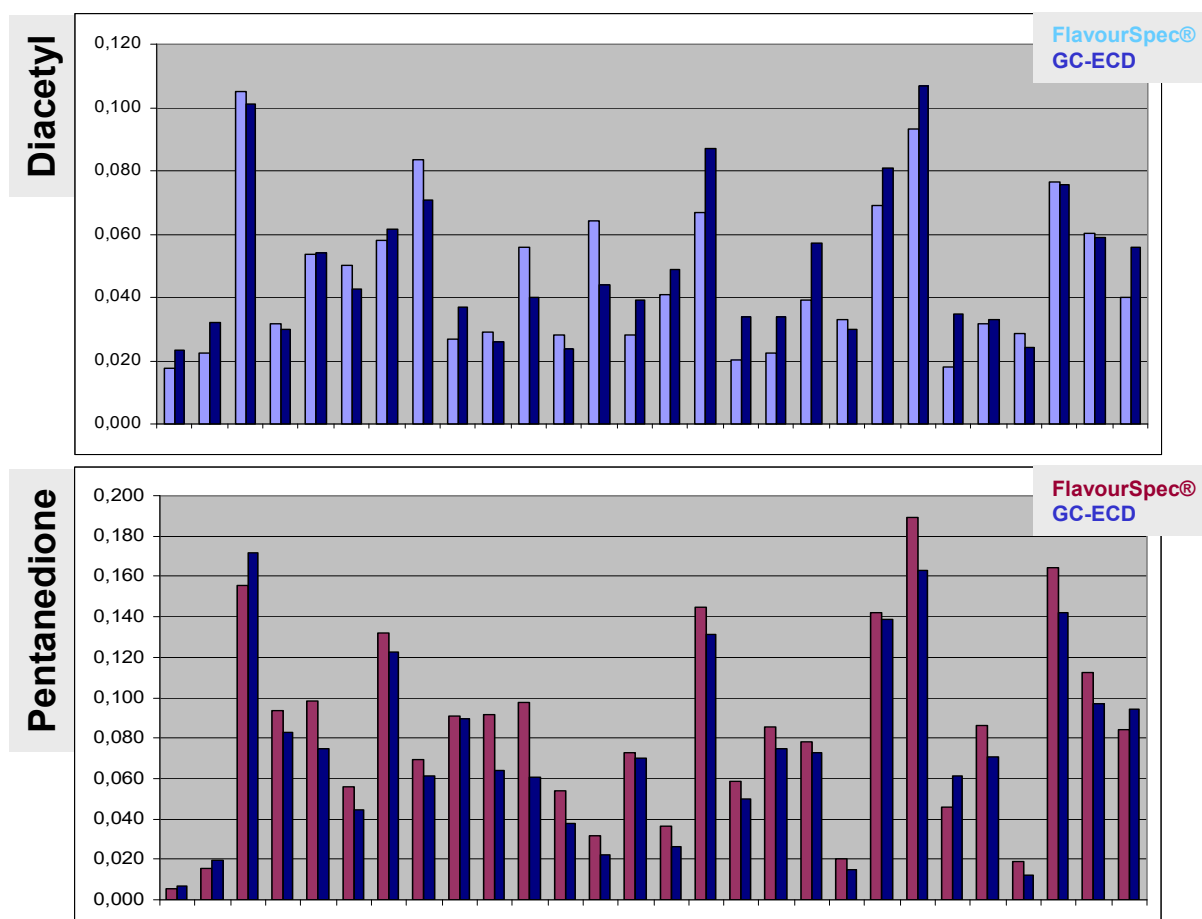


Figure 6: Results for diacetyl and pentanedione in beer samples taken from a fermentation tank using FlavourSpec® compared to a GC-ECD

Summary

FlavourSpec® is a validated analytical tool for the quantitative determination of diacetyl and pentanedione in beer using the headspace method in the concentration range of 0.01 up to 0.5 mg/L with an outstanding reproducibility and accuracy. It is easy-to-use, maintenance costs are low and compared to an ECD due to radioactive regulation no licence is required.

As a very attractive add-on FlavourSpec® allows to determine flavour active and quality marking compounds with just one click by using the positive ionisation mode of the IMS. By that commodities like hops or finished products can impartially be authenticated and tested with respect to their flavour and/or quality.