

# GC/MS Application Note



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GC-MS determination of stale aldehydes  
in beer by SPME on-fibre derivatization



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# GC-MS determination of stale aldehydes in beer by SPME on-fibre derivatization

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## Abstract

This article describes the determination of stale aldehydes in beer, such as 2-methyl-propionaldehyde, 3-methyl-butylaldehyde, 2-methyl-butylaldehyde, valeraldehyde, caproaldehyde, furaldehyde, phenylacetaldehyde by SPME/GC-MS. The aldehyde compounds are derivatized with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) using an on-fiber derivatization procedure. After adsorbing PFBHA onto a 65  $\mu\text{m}$  PDMS/DVB fiber, it is inserted into a 20 mL sample vial containing a 2 mL beer sample in the agitator at 60  $^{\circ}\text{C}$  for 60 min. Extraction and derivatization are both controlled by the PAL autosampler. The analytes are detected by GC-MS operated in selective ion monitoring mode on the characteristic mass  $m/z$  181.8 for carbonyl compounds, delivering a wide linear range of in 0.2 to 500  $\mu\text{g/L}$ . The coefficient of correlation for the quantitative calibration is better than 0.99. The precision of the method is characterized with RSDs between 1.0 % - 15.7 %. The recoveries are between 88 % - 107 %. This method proved to be suitable for the study on the beer refreshing period during product quality control.

## Keywords:

beer, aging, taste, aldehyde, SPME, on-fiber derivatization, PFHBA

## Introduction

A main quality problem of beer is the change of its sensory characteristics over time. After packaging beer begins to lose the fresh, perfect, pure flavor and taste over time. The beer develops a "cooked" taste or "oxidized" flavor. Currently, beer aging has become a bottleneck which is restricting the development of the beer industry worldwide. Beer aging is mainly caused by the formation of volatile aldehydes such as 3-methyl-butylaldehyde, 2-methyl-propionaldehyde, etc. [1]. It is important to develop a sensitive and reliable method to study beer aging.

The method described in this PAL application note is based on the SPME extraction with PFHBA as on-fiber derivatization reagent (Fig. 1). The quantitative GC-MS determination of stale aldehydes in beer, such as 2-methyl-propionaldehyde, 3-methyl-butylaldehyde, 2-methyl-butylaldehyde, valeraldehyde, caproaldehyde, furaldehyde, phenyl-acetaldehyde can be used for the research on anti-aging beer and product quality control [2].

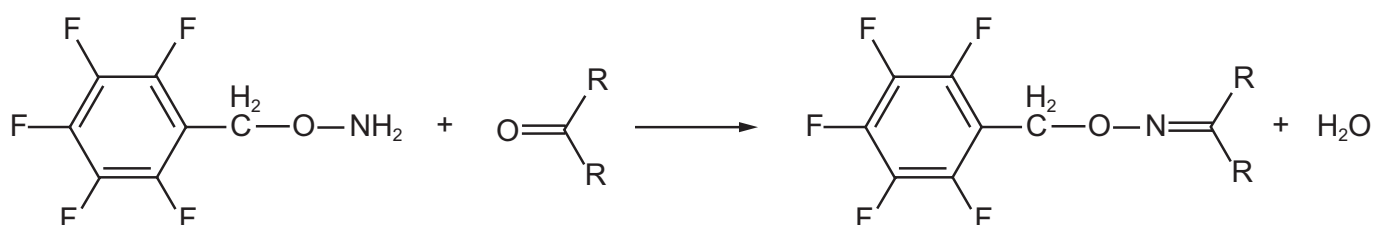


Figure 1: Reaction of PFBHA with aldehydes or ketones to form an oxime

## Instrumentation

PAL3 System and COMBI PAL  
SPME fibers: 65 µm PDMS/DVB fiber  
GC-MS: Agilent 6890/5973 MSD  
Column: DB-5 capillary (30 m, 0.25 mm i.d, 0.25 µm)

## Chemicals

**Standards** were purchased from Sigma Aldrich: 2-methyl-propionaldehyde, 3-methyl-butylaldehyde, 2-methyl-butylaldehyde, valeraldehyde, caproaldehyde, furaldehyde, phenylacetaldehyde, PFHBA

**Solvents** were purchased from Fisher Scientific: HPLC grade methanol, purified water

## Workflow

### Derivatization conditions:

Insert the fiber into the PFHBA solution (60 mg/L) at 60 °C, adsorption for 10 min.

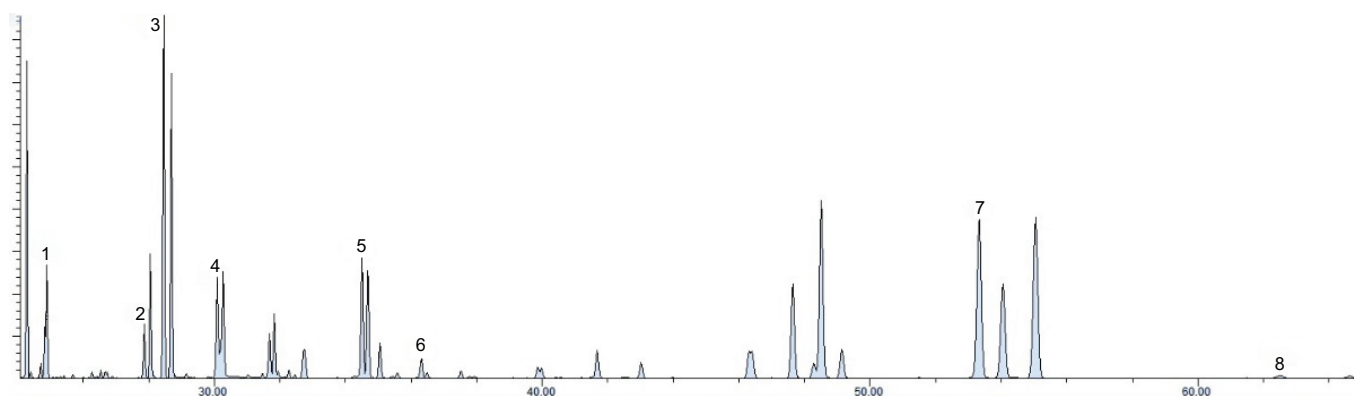


Figure 2: Total ion chromatogram of standard aldehydes with SPME on-fiber PFBOA derivatization

- |                             |                           |                           |                  |
|-----------------------------|---------------------------|---------------------------|------------------|
| 1: 2-Methyl-propionaldehyde | 2: 3-Methyl-butylaldehyde | 3: 2-Methyl-butylaldehyde | 4: Valeraldehyde |
| 5: Caproaldehyde            | 6: Furaldehyde            | 7: Phenylacetaldehyde     | 8: E-2-nonenal   |

### Sampling:

Insert the SPME fiber after loading with derivatization reagent into the headspace of a 20 mL autosampler vial, filled with 2 mL of a beer sample.

### GC Parameter:

Carrier gas: He  
GC inlet temp: 250 °C  
GC constant flow: 1.1 mL/min  
Splitless injection

### Oven temperature program:

60 °C, 2 min  
5 °C/min to 170 °C  
1 °C/min to 190 °C  
190 °C, 25min

### Sample volume selection:

The CO<sub>2</sub> bubbles of the fresh beer were removed manually at room temperature before filing the HS vials. The repeatability and precision of the method was checked with sample amounts of 2 mL, 5 mL and 10 mL. Beer samples of 2 mL in 20 mL vials gave the best performance.

### Detection limits and correlation coefficients:

A standard calibration was used in the range 0.2-500 µg/L (see Tab. 1).

Compounds	Detection Limits (µg/L)	Correlation Coefficients
2-Methyl-propionaldehyde	0.05	0.992
3-Methyl-butylaldehyde	0.04	0.994
2-Methyl-butylaldehyde	0.02	0.993
Valeraldehyde	0.12	0.990
Caproaldehyde	0.07	0.991
Furaldehyde	10.0	0.997
Phenylacetaldehyde	0.02	0.997
E-2-Nonenal	0.002	0.990

Table 1: Detection limits (S/N > 3) and correlation coefficients

### Fiber selection:

From a comparison of PDMS/DVB (65 µm), CW/DVB (65 µm), and Polyacrylate (85 µm) the PDMS/DVB (65 µm) fiber material was chosen as the best one.

### Extraction time and temperature:

After testing, 60 °C for 60 min incubation time was found to be most suitable for beer samples and could provide a good balance for all the test compounds.

### GC-MS conditions:

El Source: 70 eV  
Interface temp: 250 °C  
Source temp: 230 °C  
Quadrupole temp: 150 °C  
Scan range: 50-550 Da

## Results

### Precision and Recovery

Table 2 shows the results for fresh beer and beer after 6 months of aging, 5 bottles analysed each. Aldehyde standards were added to the samples to quantify the recovery. The content of the different aldehydes in stale beer was found higher than in fresh beer except for E-2-nonenal (recovery >84 %), the recoveries are between 88 % -103 %.

Compounds	Fresh beer pl (µg/L)	RSD %	Stale beer pl (µg/L)	RSD %
2-Methyl-propionaldehyde	3.4	3.7	19.5	3
3-Methyl-butyraldehyde	5.1	2.1	10.7	2.3
2-Methyl-butyraldehyde	6.2	3.3	15.4	1
Valeraldehyde	1.6	5.6	3.5	4.8
Caproaldehyde	1	4.5	1.8	2.2
Furaldehyde	53	7.1	96	7.6
Phenylacetaldehyde	5.2	7.2	9.4	8.3
E-2-nonenal	0.03	15.7	0.51	11.2

Table 2: Precision (n=5) and concentration of aldehydes in fresh and stale beer

## Conclusion

The obvious advantage of the SPME/GC-MS method to analyze stale aldehydes in beer gives a rapid extraction and better separation with small sample volumes. It is a very suitable solution for the monitoring of the status of beer aging and keep it as its best quality.

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## Comparison of SPME with liquid/liquid extraction (LLE)

Samples containing higher amounts of 2-hydroxyl-3-butanone will show interferences with the separation of the aldehydes and affect the sensitivities if the extraction is done by LLE (Fig.3). This effect is avoided by using the described headspace SPME method.

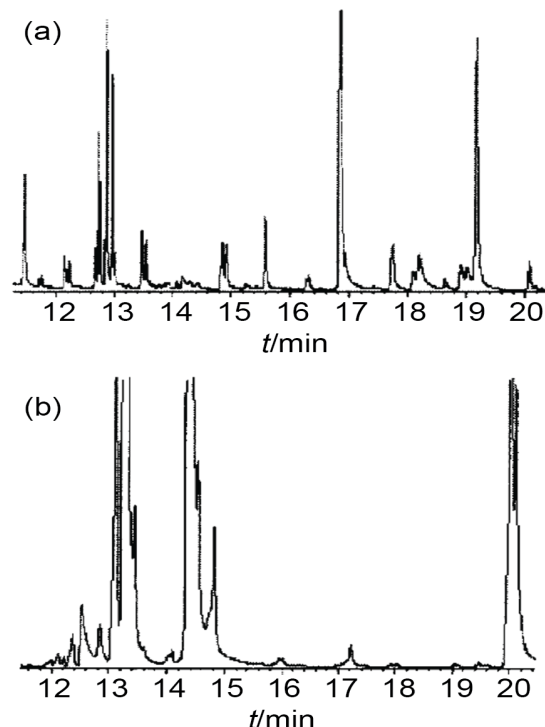


Figure 3: Comparison of (a) SPME/GC-MS and (b) LLE/GC-MS

## Reference

- [1] Vanderhaegen B. et al., The chemistry of beer aging-a critical review, Food-Chem. (2006) 95, 357-381.
- [2] Wu Q., Chen H., Yang Z., The automated headspace SPME GC-MS method for the analysis of beer aging, Chin. J. Anal. Lab. (2007) 26/4, 38-41.

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