Evaluation of Concentration Profiles from Beer-Ageing Compounds by Exploratory Data Analysis

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Introduction

Taste and flavour of beer change during storage.

The speed of ageing depends on the storage conditions and the composition of the beer.

Carbonyl compounds are essential in this process.

In this work* the concentrations of aldehydes, ketones and esters have been measured in beer samples from breweries in Austria, Hungary and Romania.

Data were obtained from fresh samples as well as from artificially aged samples.

Univariate and multivariate exploratory data analyses were applied
(1) to characterize beer from different breweries,
(2) and to compare fresh and aged beer.

* Varmuza K., Steiner I., Glinsner T., Klein H.:
Chemometric evaluation of concentration profiles from compounds relevant in beer ageing.
Eur. Food Res. Technol., **215**, 235-239 (2002)

Experimental

Beer samples

43 samples (Lager beer, Pils beer, some special beers) from 14 breweries (Austria: 8, Hungary: 2, Romania: 4).

Fresh samples: storage 14 days at 10°C.
Artificially aged samples: storage 3 days at 45°C.

Analysis

Steam distillation. Then GC/MS or HPLC.

Compounds

No	Name	CAS Reg.No	Formula	Method
1	**3-methyl-butyraldehyde**	590-86-3	$C_5H_{10}O$	GC/MS
2	**3-methyl-2-butanone**	563-80-4	$C_5H_{10}O$	GC/MS
3	**2-methyl-butyraldahyde**	96-17-3	$C_5H_{10}O$	GC/MS
4	**capronaldehyde**	66-25-1	$C_6H_{10}O$	GC/MS
5	**2-(hydroxymethyl)-furan**	98-00-0	$C_5H_6O_2$	GC/MS
6	**heptaldehyde**	111-71-7	$C_7H_{14}O$	GC/MS
7	**2-furyl methyl ketone**	1192-62-7	$C_6H_6O_2$	GC/MS
8	**5-methyl furfural**	620-02-0	$C_6H_6O_2$	GC/MS
9	**furfuryl acetate**	623-17-6	$C_6H_6O_3$	GC/MS
10	**2-acetyl-5-methyl furan**	1193-79-9	$C_7H_8O_2$	GC/MS
11	**benzene acetaldehyde**	122-78-1	C_8H_8O	GC/MS
12	**nicotinic acid ethylester**	614-18-6	$C_8H_9NO_2$	GC/MS
13	**ethyl phenylacetate**	101-97-3	$C_{10}H_{12}O_2$	GC/MS
14	**gamma-nonanoic lactone**	104-61-0	$C_9H_{16}O_2$	GC/MS
15	**furfural**	98-01-1	$C_5H_4O_2$	GC/MS
16	**5-hydroxymethyl-2-furancarbox-aldehyde**	67-47-0	$C_6H_6O_3$	HPLC

Software

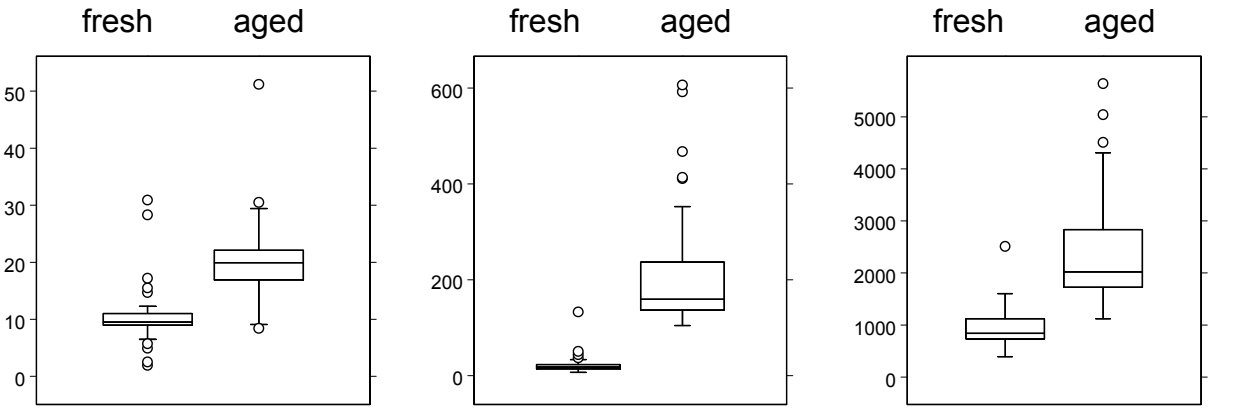
Software *Axum* (Mathsoft Inc., Seattle, WA, USA), software *SCAN* (Minitab Inc. State College, PA, USA), and own software.

Results (1)

Most substances exhibit a **great span** of their concentrations in fresh beer as well as in aged beer. For all substances the concentration ranges of fresh and aged beer overlap.

The paired *t-test* was applied to find compounds that show a significant **increase of the concentrations in aged beer**.

Box plots for three of these compounds



nicotinic acid ethylester (no **12**)

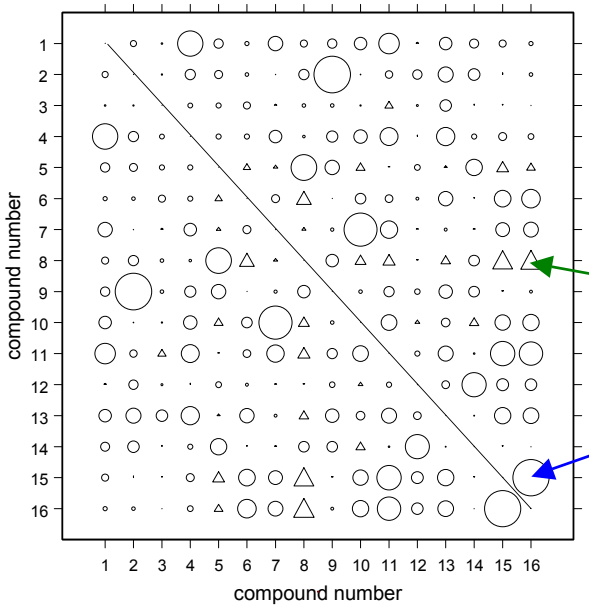
furfural (no **15**)

5-hydroxymethyl-2-furancarboxaldehyde (no **16**)

concentrations in µg/l

Correlation coefficients between concentrations

Calculated from all data (43 beer samples, fresh and aged)



Size of symbols is proportional to the absolute value of the correlation coefficient.

Positive values are denoted by circles, negative values by triangles.

***r* = - 0.54**

***r* = + 0.90**

Highly correlating compounds (**2, 7, 9, 10, 15, 16**) are products from the **Maillard reaction**.

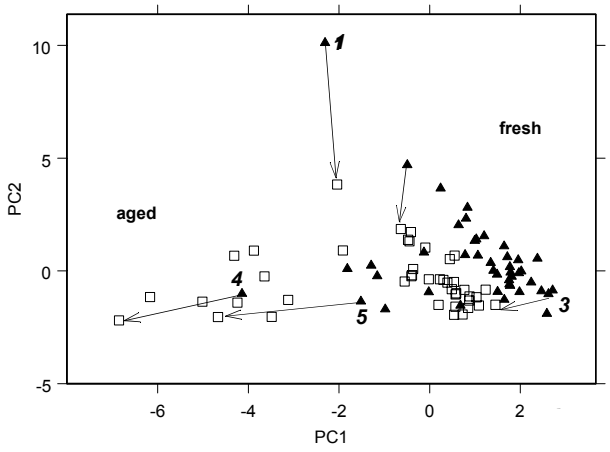
Results (2)

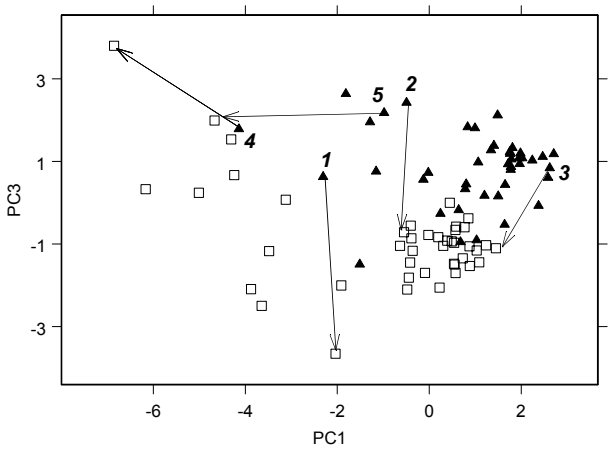
PCA with all data

Data

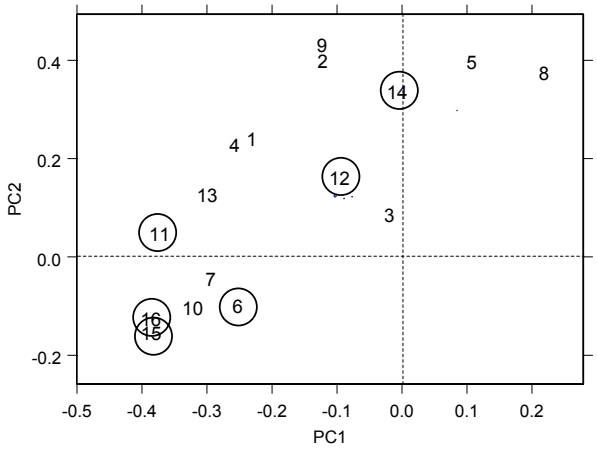
Objects: 43 fresh samples + 43 aged samples
Features: 16 concentrations (autoscaled)

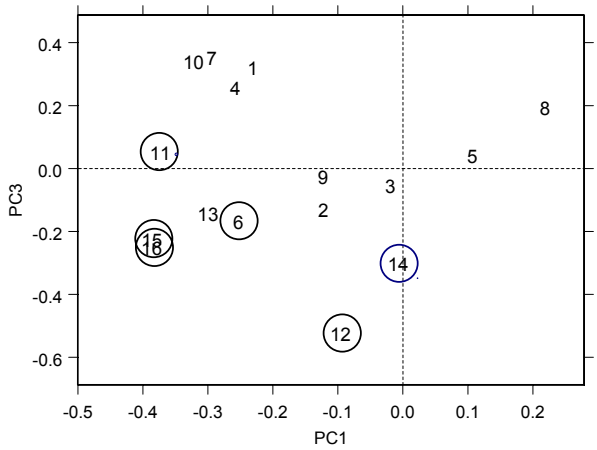
Score plots





Loading plots





PC1, PC2, PC3 are the scores of the 1st, 2nd, and 3rd principal component (variances are 27.1, 19.5, and 11.9 % of total variance).

▲ **fresh** beer samples
☐ artificially **aged** beer samples

Arrows connect corresponding fresh and aged samples (five examples).

Encircled numbers are substances with significantly increased concentrations in the aged samples.

☞ **Fresh and aged samples are - in general - well separated.**

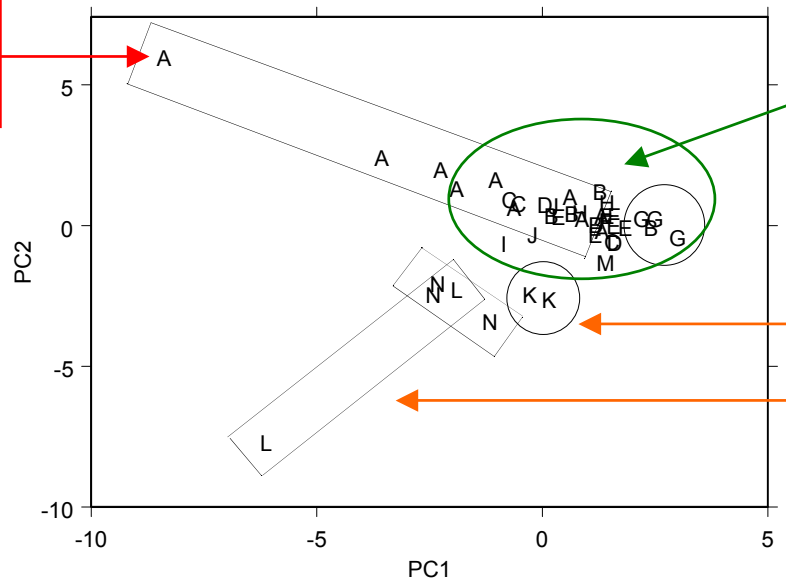
☞ **However, some of the fresh beer samples are located in the area which is typical for aged samples.**

☞ **Result corresponds to experiences obtained from organoleptic tests.**

Results (3)

PCA with data from fresh beer samples

„outlier“:
Festbock-Bier
(a strong beer)



area for typical (good) fresh beer

fresh beer from these breweries is very different from others

Objects: 43 fresh beer samples; features: 16 concentrations (autoscaled).
Variances preserved: PC1, 30.7%; PC2, 23.7% of total variance.

A - H	Austrian breweries	I - J	Hungarian breweries
		K - N	Romanian breweries

Conclusions

- **Concentration profiles of the measured 16 compounds contain information about type and quality of fresh beer.**
- **PCA is able to find clusters of similar beer samples and to detect outliers.**

“Taste and aging of beer are phenomena that are multivariate in nature”

Siebert K.J.: Chemometrics in brewing - a review.
J. Am. Soc. Brew. Chem. **59,** 147-156 (2001)