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Engineering investigations of the recreating kinetics of flavour-components during the boiling of wort

An important effect of boiling wort is the recreation of aromatic compounds. Unwanted flavour-components are not only expelled, they are also recreated during the boiling of wort and the whirlpool rest. There are different opinions on which flavour-components are significantly recreated during the boiling of wort. Because of this, the aim of the research was to see which aromatic compounds go through a significant recreation at wort boiling temperatures and, thus, possibly during the whirlpool rest, too. On account of this the creation rates of unwanted flavour-components are measured in a closed reactor with a reflux condenser in order to inhibit calcination and thus get reliable results. After samples are taken at defined time intervals, they are immediately cooled down and analysed by gas chromatography (GC). This way the increase of flavour-components is measured and rate constants are acquired. To get a wide spectrum of different wort flavour-components the measurements were done for 2-Methylbutanal (2MB), 3-Methylbutanal (3MB), Phenylethanal, Benzaldehyde, 2-Furfural, γ-Nonalactone, Hexanal, 2-Phenylethanol and Dimethylsulfide (DMS) respectively S-Methylmethionine. These are important flavour-components that have to be reduced to below a defined level during the boiling of wort. If the calcination of these compounds, especially of DMS, is insufficient, off-flavour will occur in the resulting beer. This would also implicate worse flavour stability.

The described method is able to determine the rate constants of the recreation of wort flavour-components. The results confirm the theory, that aroma compounds from fatty acids are not recreated during the boiling of wort and thus are not created in the whirlpool, either. For some compounds of the Strecker-degradation this is also applicable at current wort boiling times. For 2-Furfural and DMS the recreation must be implicitly considered.

The new measurement results can be used to make a detailed prediction of the recreation of unwanted wort aroma compounds during the boiling of wort and the whirlpool rest.

The main reason why these trials were done is that the results are needed for the calculation of exact residue curves of wort flavour-compounds during the boiling of wort. Residue curves can be calculated if the vapour-liquid-equilibrium of the flavour-components is known. In opposite to residue curves of flavour-components in pure water, where no recreation takes place, a possible recreation of compounds during wort boiling must be considered in the calculation of these curves in wort. Therefore rate constants are only measured at the atmospheric boiling temperature of wort for the purpose of this article. The results of this article are used for a planned follow-up article in this magazine, which discusses the steaming behaviour of the same flavour-components.

Descriptors: wort boiling, whirlpool, rate constants, flavour-components, flavour stability

1 Introduction

Due to the high temperatures during the boiling of wort, unwanted aromatic compounds are recreated in different amounts depending on their way of creation. At former boiling times of more than 90 min. the recreation during the boiling was sufficient to avoid a significant recreation in the whirlpool. As in nowadays the recreation time in the wort kettle is insufficient, unwanted aromatic compounds can be recreated further on in the whirlpool, too. These flavour-components can only be reduced after the whirlpool stage with an accessorily evaporation. This additional evaporation would also induce a decrease in desirable hop components and thus the utilization. Thus and because of the necessary additional evaporation energy, it is advantageous to avoid this step.

One of the most important aroma compounds that have to be reduced during the boiling of wort is Dimethylsulfide. The paramount recreation mechanism of this flavour-component is the thermal degradation of S-Methylmethionine (SMM). This and the other recreation mechanisms of DMS during the production of wort are well known and have been previously described in detail together with the characteristics of DMS [1-3]. If the total amount of DMS and SMM in beer is higher than 100 µg/l the flavour becomes cabbage- or vegetable-like [4]. It has been shown that the amount of this component in wort after the boiling process can still be found in the final beer [5]. Because of the importance of this flavour-component in the production of beer, the recreation of DMS is investigated in this article.

Unfortunately, at this time there is little known about the recreation kinetics of other wort aroma compounds at normal boiling temperatures, and opinions about their significance differ.

There are two primary ways of the recreation of other wort aroma compounds, and both have recently been described in detail [6-8]: the lipid metabolism and the Maillard-reaction including the Strecker-degradation [9]. While nearly all authors agree about the fact that aroma compounds of the lipid metabolism are only significantly recreated during the malting process and not during the wort boiling process [6, 7], their opinion about the recreation

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Figures see Appendix.

of aromatic compounds of the Strecker-degradation differs. Most authors in the brewing sector claim that flavour-components of the Strecker-degradation are significantly recreated during the boiling of wort [6, 7, 10]. Other authors of food sciences claim that the Strecker-degradation in liquids is negligible. Cremer [11] investigated the recreation of Strecker-aldehydes in dry paprica powder and its aqueous suspension. His finding was that the recreation in aqueous suspensions is not significant over short time periods. This is due to the high dilution of the reactants and also to the fact that water is a product (*c(X)*) of the Maillard-reaction. Therefore the equilibrium concentration of the reactants is more situated on the educt (*c(A)*) side. Cremer [11] also showed that an effect of the pH-value on the recreation at a value in the range of wort is negligible, too. Fritsch [12] showed that the Strecker-degradation is of circumstantial importance during the wort boiling process and thus during the whirlpool rest also.

The investigated flavour-components of the Maillard-reaction were 2-Methylbutanal (2MB) (flavour: sweetish malty [13]), 3-Methylbutanal (3MB) (flavour: dull malty [6]), Phenylethanal (flavour: honey-like [6]), Benzaldehyde (flavour: bitter almond [14]; cherry [15]) and 2-Furfural (dull malty [6]; paper-like, oxidised [16]). These components are jointly responsible for the ageing process of beer [6]. It is proven that there is a correlation between an ageing-flavour and an increase of these components [17].

The investigated flavour-components of the lipid-metabolism were γ-Nonalactone (flavour: coconut [18]) and Hexanal (flavour: dull malty [19]; tallowy, petalled [15]). These components have the same influence on the ageing of beer as the components of the Maillard-reaction [19].

All those carbonyl-compounds are responsible for a wort-like smell that has to be exhaled during wort boiling.

In addition to these components, 2-Phenylethanol (flavour: flowery [6]) was also investigated. 2-Phenylehanol is the corresponding alcohol to Phenylethanal. This higher alcohol also figures in the ageing of beer and can be oxidised to Phenylethanal [13].

All investigated flavour-components must be thoroughly evaporated during the boiling of wort to avoid an off-flavour in the resulting beer and to get a good flavour stability [6].

To gain knowledge about which aromatic compounds are significantly recreated at the atmospheric boiling temperature of wort, their recreation kinetics are analysed in this work.

2 Materials and methods

Fundamentals

The field of reaction kinetics is concerned with the rates and mechanisms of chemical reactions. It considers relations between the rate of a reaction and the concentration of reactants. The reaction rate for a reactant or product in a particular reaction is defined as the amount per unit per time per volume that is formed or removed.

Depending on the mechanisms of chemical reactions, different reaction orders occur. These orders can be of zeroth, first or higher order. Due to the order of a chemical reaction different rate constants with different units are acquired. Because of this, rate constants cannot be compared among the different reaction orders, so this is often asserted.

According to the law of Arrhenius [20], the velocity of a reaction increases strongly with increasing temperature and vice versa. Therefore, if the recreation of a flavour-component is negligible at the atmospheric boiling temperature, no recreation will take place at lower temperatures, e.g. in the whirlpool, either.

The fundamentals of reaction kinetics have previously been described in detail [20-22]. Unique insights on reaction kinetics in foods is given by Westphal et al. [23].

There are two main reaction orders for the recreation of aromatic compounds that occur during the boiling of wort and the whirlpool rest.

Flavour-components that are created following the Maillard-reaction directly from sugars [7], such as 2-Furfural, follow a zeroth order reaction. This is due to the fact, that sugars are always present in such high amounts in wort, that the velocity of the reaction is educt (*c(A)*) independent. Forster [7] demonstrated this with the example of thiobarbituric acid values (TBI) [24] in which products like 2-Furfural play a major role.

The velocity of a reaction of the zeroth order follows equation 1:

$$v = k_0 = -\frac{dc(A)}{dt} = \frac{dc(X)}{dt} \quad (1)$$

The integration with the start-concentration $c_0(A)$ at the time t_0 till the concentration $c(A)$ at the time t leads to

$$c(A) = c_0(A) - k_0 \cdot t \quad (2)$$

This is a linear equation with the slope $-k_0$. The rate constant k_0 can be acquired by the following equation:

$$k_0 = \frac{-\Delta c(A)}{\Delta t} = \frac{\Delta c(X)}{\Delta t} \quad (3)$$

The unit of k_0 is $\left[\frac{c}{t}\right]$.

Equation 2 can also be written with the start-concentration of the products $c_0(X)$ for the concentration $c(X)$ of the products at the time t.

$$c(X) = c_0(X) + k_0 \cdot t \quad (4)$$

Typical for this order of reaction is that its velocity is independent of the start-concentration of the educts $c_0(A)$. There is always the same amount of educts $c(A)$ consumed and accordingly the same amount of products $c(X)$ formed.

Aroma compounds that are created out of fatty acids such as Hexanal [7] or out of the Strecker-degradation such as 2-Methylbutanal [18] follow a first order reaction [7]. This is due to the fact that fatty- or amino-acids are present in such small amounts in wort, that the velocity of this reaction depends strongly on the amount of the educts. A first order reaction is also valid for 2-Phenylethanol, which is created from a reduction of Phenylethanal [13]. The degradation of SMM and thus the creation of DMS also follows a first order reaction [25, 26].

The velocity of a reaction of the first order follows equation 5:

$$v = k_1 \cdot c(A) = -\frac{dc(A)}{dt} = \frac{dc(X)}{dt} \quad (5)$$

The integration with the start-concentration $c_0(A)$ at the time t_0 till the concentration $c(A)$ at the time t leads to

$$c(A) = c_0(A) \cdot e^{-k_1 \cdot t} \quad (6)$$

The rate constant k_1 can be acquired out of an one time logarithmic application by the following equation:

$$k_1 = \frac{-\Delta \ln c(A)}{\Delta t} = \frac{\Delta \ln c(X)}{\Delta t} \quad (7)$$

The unit of k_1 is $\left[\frac{1}{t}\right]$.

Equation 6 can also be written with the start-concentration of the products $c_0(X)$ and of the educts $c_0(A)$ for the concentration $c(X)$ of the products at the time t.

$$c(X) = c_0(A) - c_0(A) \cdot e^{-k_1 \cdot t} + c_0(X) = c_0(A) \cdot \left(1 - e^{-k_1 \cdot t}\right) + c_0(X) \quad (8)$$

Typical for this order of reaction is that its velocity depends strongly on the start-concentration of the educts $c_0(A)$. This reaction does not stop abruptly, but slowly approaches its end.

Apparatus and procedure

The creation rate of unwanted flavour-components is measured in a closed reactor with a filling quantity of 2350 ml like has been used previously by Schwill-Miedaner for kinetic measurements [25] (see fig. 1).

The reactor was closed with a glassware flange-cover with 4 grounded necks. The central neck was used to splice the reflux condenser to inhibit calcination. The condenser was connected to a water quench (JULABO F18). In a second neck a temperature probe PT100 was plugged in for measuring the boiling temperature with an accuracy of 0,1 K. The third neck was closed with a grounded plug and the last was used for sampling.

Before the kinetic measurements began, the reflux condenser and the method were checked for capability. Therefore test-solutions with equal flavour-components in the same dilution region as in wort were placed in the reactor and test-measurements were done in the way described below. As a recreation of flavour-components in the test solutions is impossible, the amount of each flavour-component should stay equal over the whole time, providing the dimensions of the condenser are adequate and there is no effect of sampling on the concentration of a component in the solution. An effect of the latter is implausible as the amount of the remaining solution that has to be evaporated to fill a steam room of 500 ml is marginal.

Before the measurements started, the temperature of the reflux condenser was appointed to 1°C. Then the reactor was heated with a heating jacket to 130°C. The jacket was connected to a water quench heater (JULABO F30), which was filled with oil (THERMIA B, Shell).

After the desired temperature in the jacket and the condenser had been achieved, 2350 ml of wort were filled into the reactor and heated up. Following this the reactor was closed with the flange cover.

At the moment the wort has reached a constant temperature (alternatively its boiling point), the time observation started. After 15, 30 and 45 min. specimens of about 500 ml were taken out of the reactor and filled into a sampling bottle. To stop the reactions in the wort, the bottles were immediately cooled down in ice water.

As our chair does not possess the means to analyse the samples by gas chromatography, the sample bottles were given to the "Forschungszentrum Weihenstephan für Brau- und Lebensmittelqualität der TU München (blq)" [27].

The carbonyl-components in wort were analysed according to method "PVGC 022" and the increase or decrease of wort flavour-components over the time t was attained. The analysis method "PVGC 022" is a proven and standard method for the analysis of wort aroma compounds at the blq and is described in detail elsewhere [15, 28, 29].

A brief description of method "PVGC 022" together with the GC parameters is given in the following:

The volatile compounds of wort are enriched by steam distillation and extracted with dichloromethane. Afterwards, the solvent phase is analysed gaschromatographically using a flame ionization detector (FID). The verification of the detector's linearity and the determination of the concentration occurs via several concentration levels within the relevant area, under evaluation of the relative peak areas. Figure 2 shows a demonstration of a chromatogram for carbonyl components in wort:

GC parameters:

GC:	Perkin Elmer Autosystem XL with FID		
column:	M&N optima-5ms 60m*0,25mm*0,25µm		
temperature programme:	40°C	10min	2°C/min
	150°C	1 min	45°C/min
	250°C	3 min	
injector temperature:	250°C		
detector temperature	300°C		

DMS and SMM were analysed according to "MEBAK III" at the same institute (blq). The method used to analyse DMS and SMM is also a proven and standard method at the blq and has previously been described in detail [30].

A brief description of the method "MEBAK III" together with the GC parameters is given in the following:

DMS in wort is also analysed gaschromatographically using head space technique, this time together with a flame photometer detector (FPD). The determination of the concentration occurs via several concentration levels within the relevant area, under evaluation of the relative peak heights. Figure 3 shows a demonstration of a chromatogram for DMS in wort including an internal standard:

GC parameters:

GC:	Perkin Elmer Auto System XL with FPD
column:	M&N Optima 5 30m*0,53mm*3,0µm
temperatures:	
- oven:	90°C isotherm
- injector:	120°C
- detector:	250°C

Head-Space parameters Perkin Elmer HS 40:

sample temperature:	70°C
transfer temperature:	110°C
needle temperature:	100°C
cycle time:	1,6 min.
thermostating time:	30,0 min.
pressuration time:	1,0 min.
injection time:	0,04 min.
withdraw time:	0,2 min.
vent:	yes

In order to achieve a wide spectrum of different wort flavour-components, measurements were taken for the Maillard-reaction-products 2-Methylbutanal (2MB), 3-Methylbutanal (3MB), Phenylethanal, Benzaldehyde and 2-Furfural as well as for the lipid-metabolism products γ-Nonalactone and Hexanal. The measurements were also performed for the higher alcohol 2-Phenylethanol and for the sulfur compound Dimethylsulfide, respectively S-Methylmethionine. These measurements were performed individually at least 3 times in order to obtain statistic reliability.

As the only interest in the results of the measurements was to gain knowledge about which flavour-components are significantly recreated at wort boiling temperatures, no investigations about the activation energies of the different reactions were undertaken.

If a recreation of a flavour-component occurs during the boiling of wort, this recreation must also be considered for the calculation of its residue curve.

To confirm the theory of Arrhenius [20] for a brewery, trials in a whirlpool at lower temperatures were undertaken. These tests had the sense to show that those flavour-components that are not recreated at wort boiling temperatures are also not rebuilt significantly during the whirlpool rest, were the temperatures can be about 10 K lower. Therefore 300 l wort were boiled in a "Merlin® wort kettle" according to a standard process and afterwards the wort was analysed at the beginning and at the end of a whirlpool rest (WP) of 30 min..

The Merlin ® pilot plant used is dimensioned for 2 - 3,5 hl wort. The pump used has a maximum capacity of 2800 l/h and the maximum steam pressure is 3 bar.

These measurements were also performed at least 3 times and the samples were analysed in the same laboratory (blq) according the methods "PVGC 022" and "MEBAK III" respectively.

3 Results and discussion

The results obtained from the test-solutions show that the amount of flavour-components in the reactor stayed equal over the whole measurement period. Thus it can be assumed that the dimensions of the condenser are adequate and that the sampling has no influence on what amount of the flavour-components in the wort stays in the reactor.

The results of the kinetic measurements confirm the theory of Fritsch [12] and Cremer [11] and show significant recreations for 2-Furfural and Dimethylsulfide only (see figures 2-10). For all other flavour-components of the Strecker-degradation and for the ones that are created from fatty acids, no significant increase of their concentration c was measured. This is also valid for 2-Phenylethanol.

Due to these results, only rate constants for 2-Furfural and DMS were acquired.

The measured values of the flavour-components over the time *t* that showed no significant increase during the measurements are shown graphically in figure 2-8 together with their confidence intervals (95 %).

Figure 11 shows the measured increase of the concentration *c* of 2-Furfural over the measured time period *t* after an outlier calculation according to Grubbs [31].

This straight line follows equation (9) with a stability index of $r^2 = 0{,}9995$.

$$c(2-Furfural) = 57{,}76 + 2{,}269 \cdot t \qquad (9)$$

The kinetic analyses gives the following zeroth order rate constant with its confidence interval (95 %) for 2-Furfural at a wort boiling temperature of 99,4 °C:

$$k_{0_{2-Furfural\ ,\ reactor}} = (2{,}269 \pm 0{,}095)\frac{\mu g}{l \cdot \min} \qquad (10)$$

The decrease of the logarithm of the concentration *c* over the time *t* of SMM is graphically plotted in figure 10.

This straight line follows equation (11) with a stability index of $r^2 = 0{,}9930$.

$$\ln c(SMM) = 6{,}224 - 0{,}0231 \cdot t \qquad (11)$$

The kinetic analyses gives the following first order rate constant with its confidence interval (95 %) for the decrease of SMM and thus for the increase of DMS at a wort boiling temperature of 99,4 °C:

$$k_{1_{SMM\ /\ DMS\ ,\ reactor}} = (0{,}0231 \pm 0{,}0022)\frac{1}{\min} \qquad (12)$$

The temperature during the whirlpool rest decreased from 99,4 °C at the beginning to approximately 90,6 °C at the end after 30 min..

The measured values of the aromatic compounds after the whirlpool rests are normalised with their corresponding initial values before the whirlpool rests and are given in proportion. The values together with their confidence intervals (95 %) are plotted graphically in figure 4.

Figure 13 shows, that the assumptions made [20] are valid and that the recreation of aroma compounds of the Strecker-degradation also plays a circumstantial role during the whirlpool rest. This also applies for 2-Phenylethanol and for the aroma compounds that are created from fatty acids.

In contrast to this, the recreation of 2-Furfural and DMS must be implicitly considered during the whirlpool rest.

4 Conclusion and summary

The results of this research show that the recreation of unwanted flavour components of the Strecker-degradation only plays a circumstantial role at wort boiling temperatures. This deviates from the theories of several authors [6, 7, 10] in the brewing sector and underlines the theory of Fritsch [12] and Cremer [11]. This is also valid for aroma compounds of the lipid metabolism and for 2-Phenylethanol. Therefore the recreation of those compounds must not be considered in the calculation of residue curves in the course of wort boiling.

In contrast to this, aroma compounds that are created directly out of sugars are significantly recreated at wort boiling temperatures. Due to this fact the recreation of 2-Furfural must be implicitly considered. This is also valid for Dimethylsulfide.

The results of the measurements of the whirlpool rests show the same results. As expected (Arrhenius [20]), the flavour-components that are not created at wort-boiling temperatures are not recreated in the whirlpool, either. This is due to the fact, that the velocity of a reaction decreases with decreasing temperature. However, the temperature in a whirlpool is still sufficient to recreate DMS and 2-Furfural significantly. As there is no way to reduce the amount of these components in further steps of the brewing process without additional evaporation, wort boiling times should be long enough to split sufficient amounts of SMM before the whirlpool rests. Another possibility is to reduce the temperature in the whirlpool in order to decelerate the recreation rates of 2-Furfural and DMS.

The results of this article will be used as the basis for a planned follow-up article in this magazine that discusses the steaming behaviour of the same flavour-components in wort. The main target of the research is the possibility to individually predict the necessary total evaporation for each brew to avoid needless intensive boiling procedures, thus saving energy and costs.

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5 Literature

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Appendix

Fig. 1 Closed reactor with reflux condenser

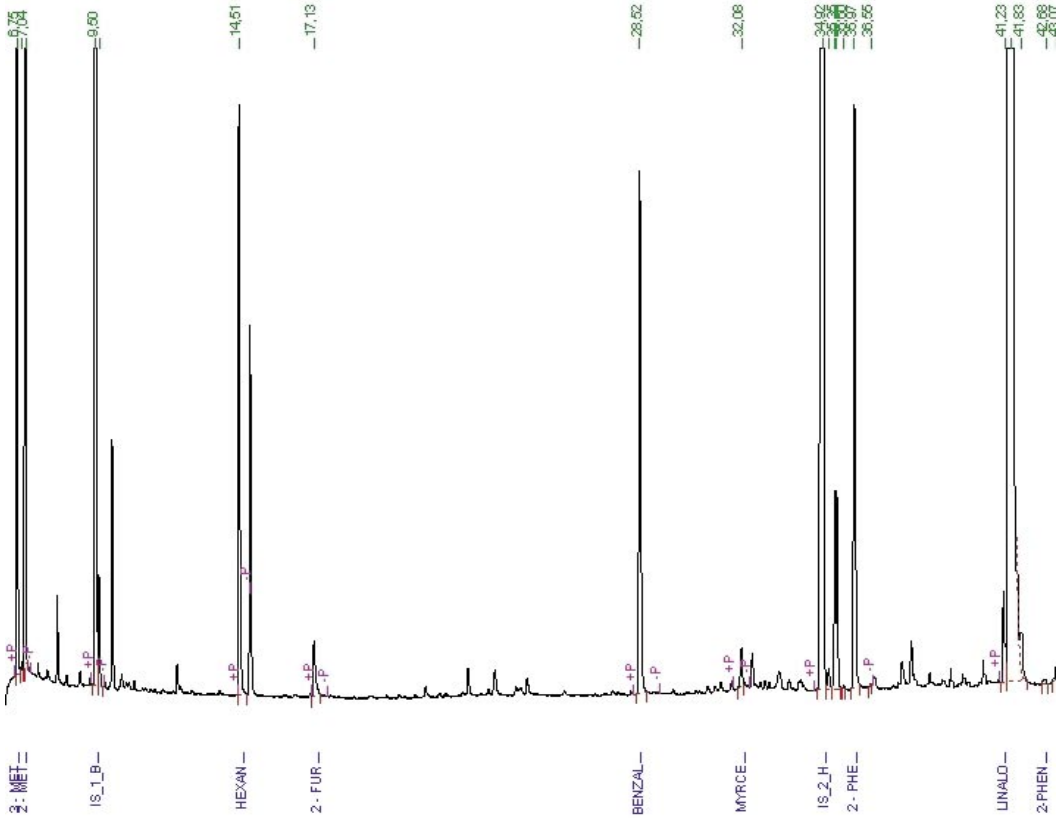

Fig. 2 Demonstration of a chromatogram of a real wort sample for wort flavour components

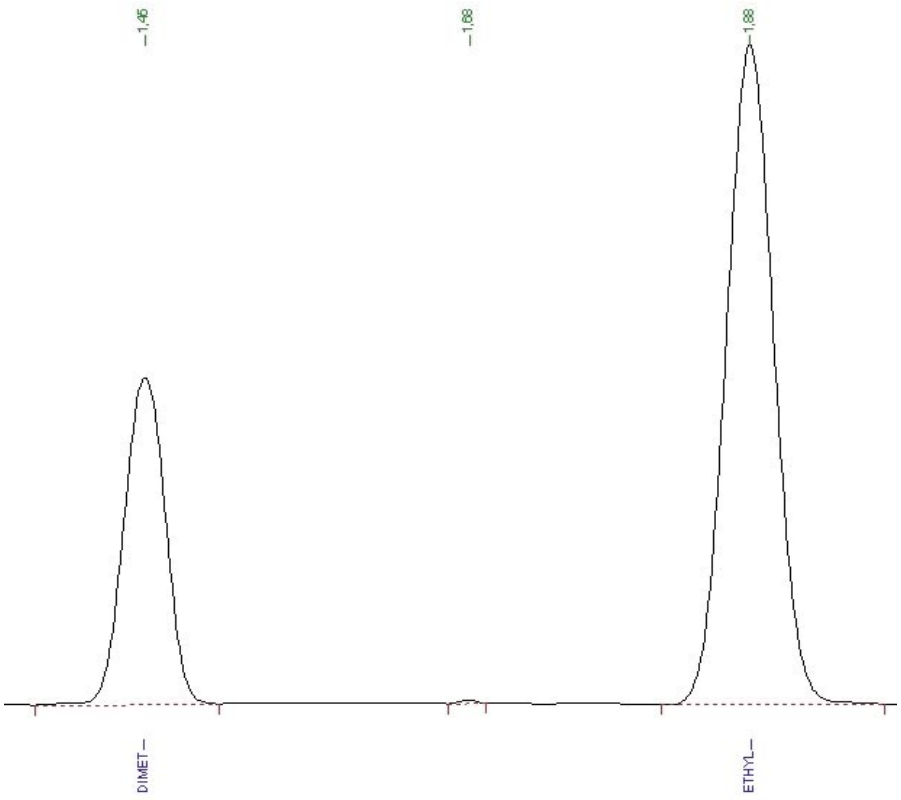

Fig. 3 Demonstration of a chromatogram of a real wort sample for DMS

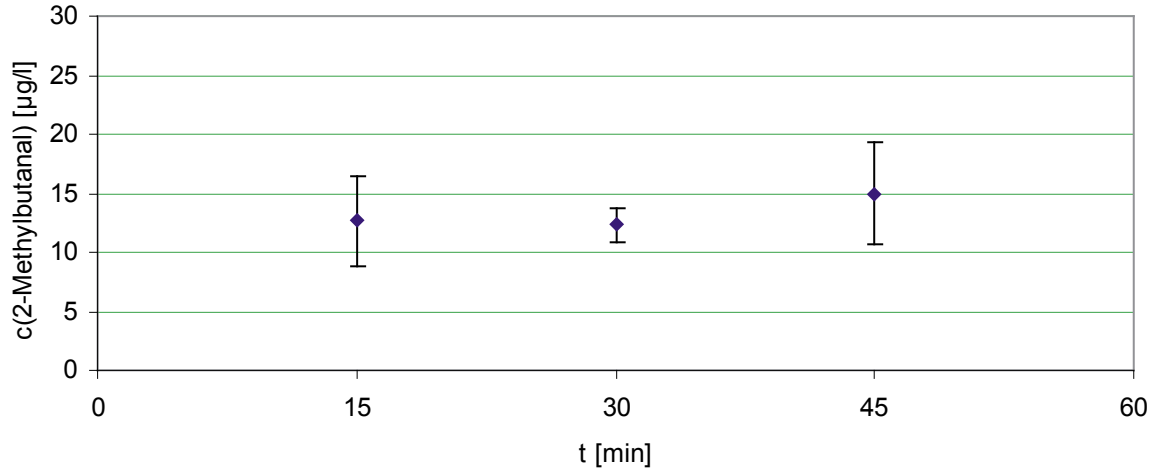

Fig. 4 Measured concentration values c of 2-Methylbutanal over a time t at 99,4 °C

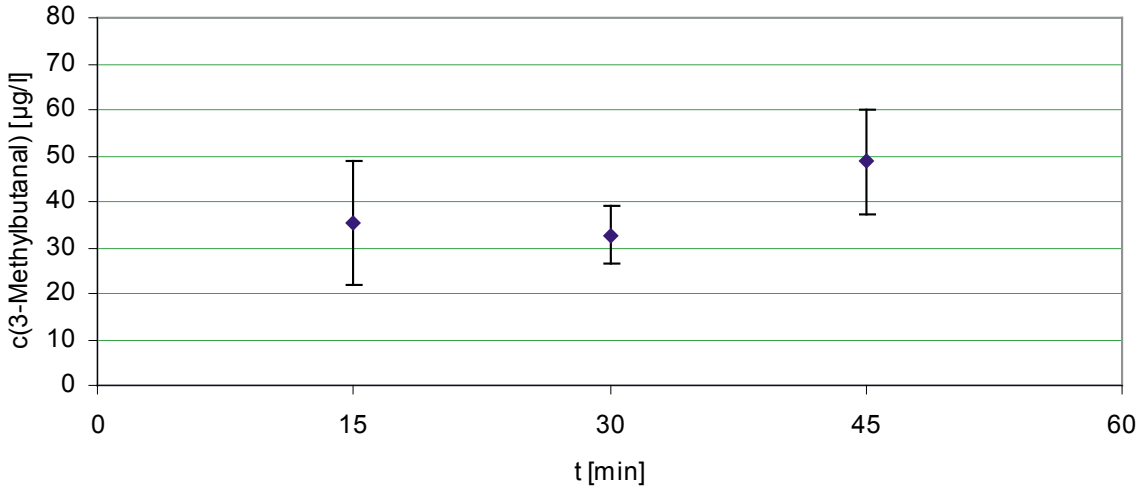

Fig. 5 Measured concentration values c of 3-Methylbutanal over a time t at 99,4 °C

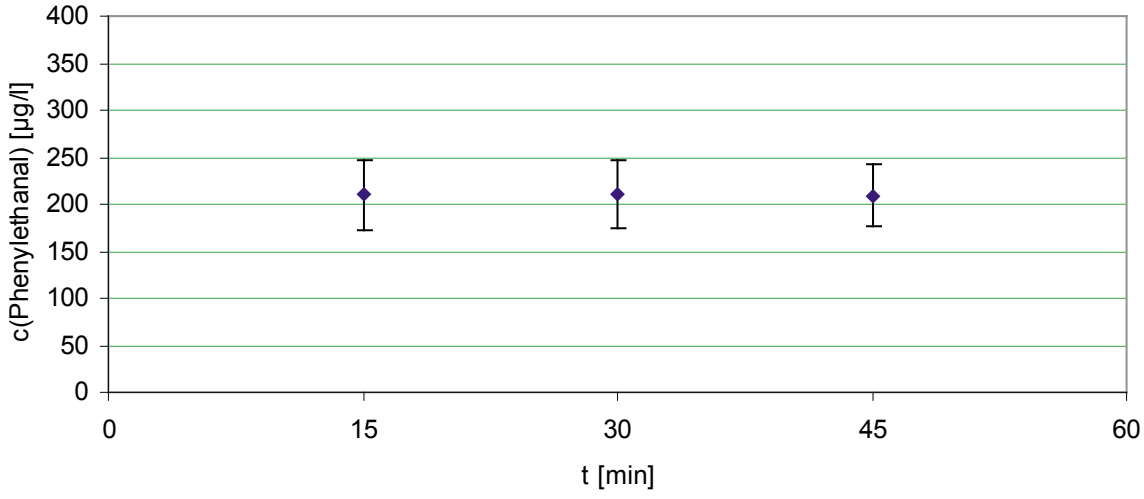

Fig. 6 Measured concentration values c of Phenylethanal over a time t at 99,4 °C

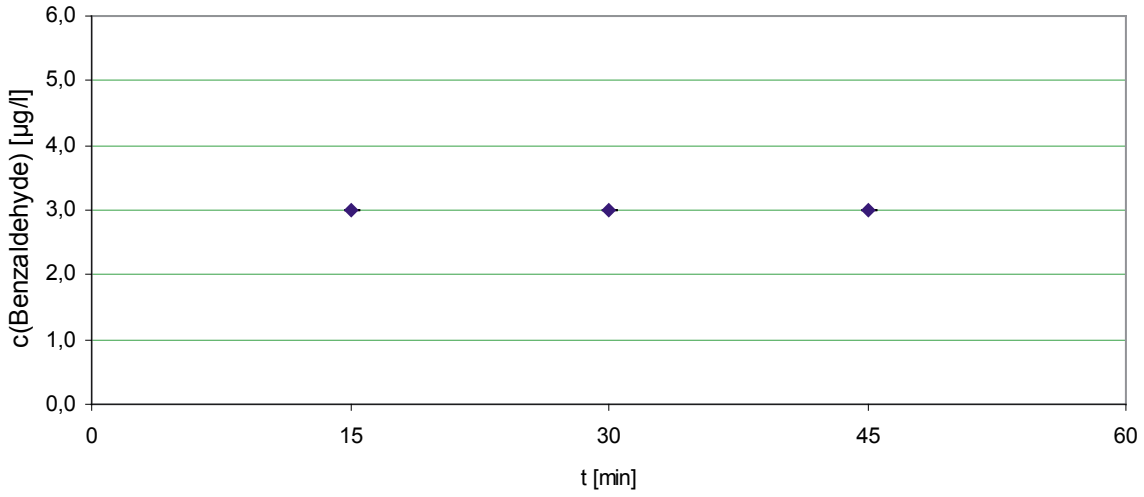

Fig. 7 Measured concentration values c of Benzaldehyde over a time t at 99,4 °C

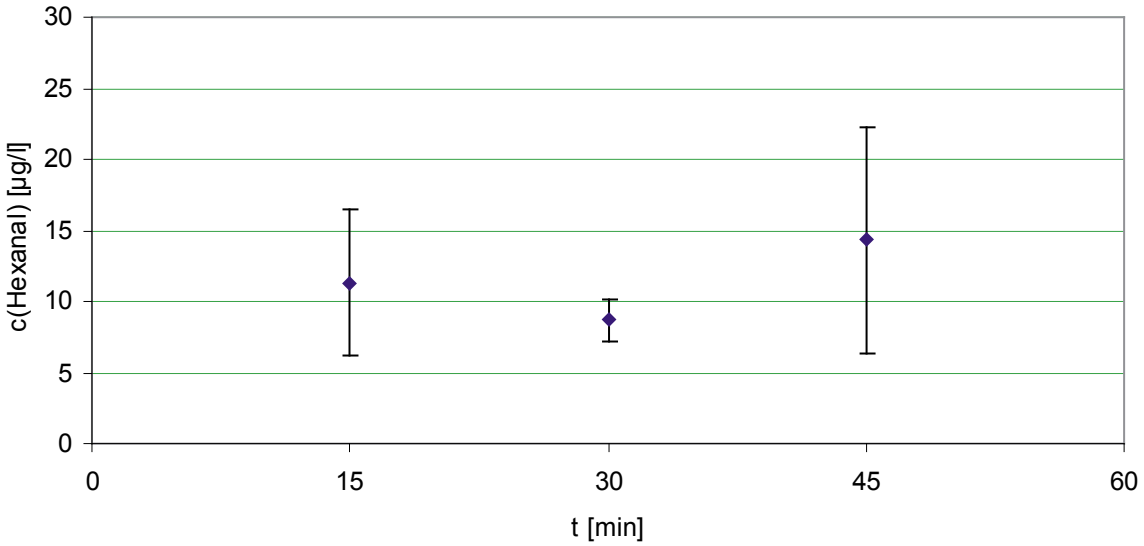

Fig. 8 Measured concentration values c of Hexanal over a time t at 99,4 °C

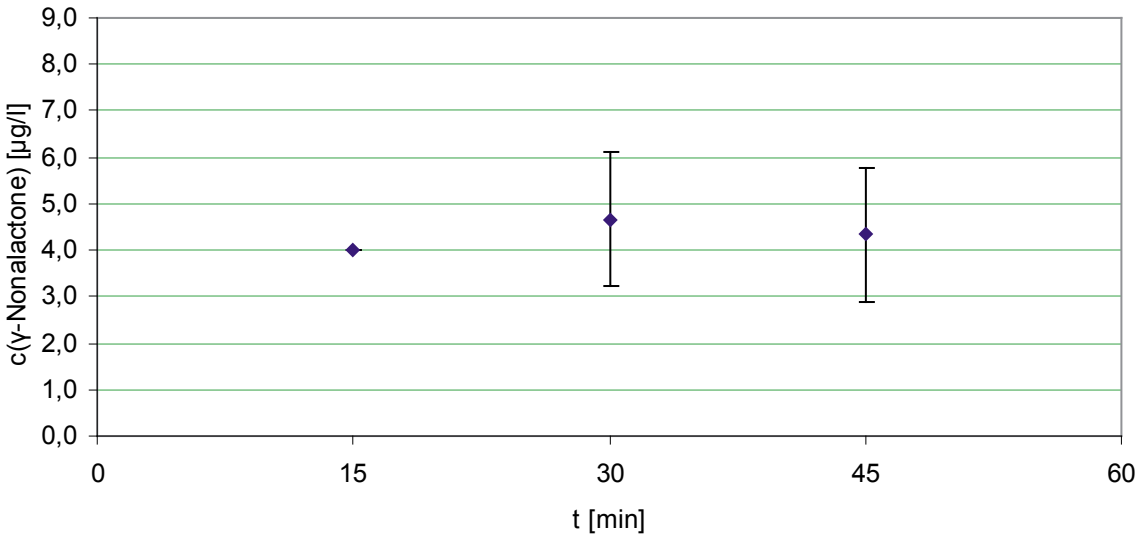

Fig. 9 Measured concentration values c of γ-Nonalactone over a time t at 99,4 °C

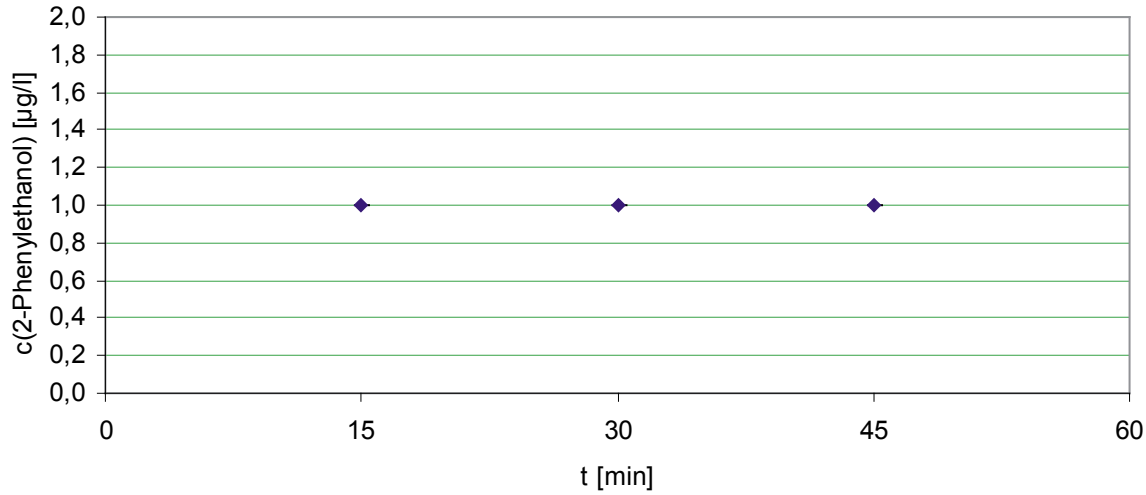

Fig. 10 Measured concentration values c of 2-Phenylethanol over a time t at 99,4 °C

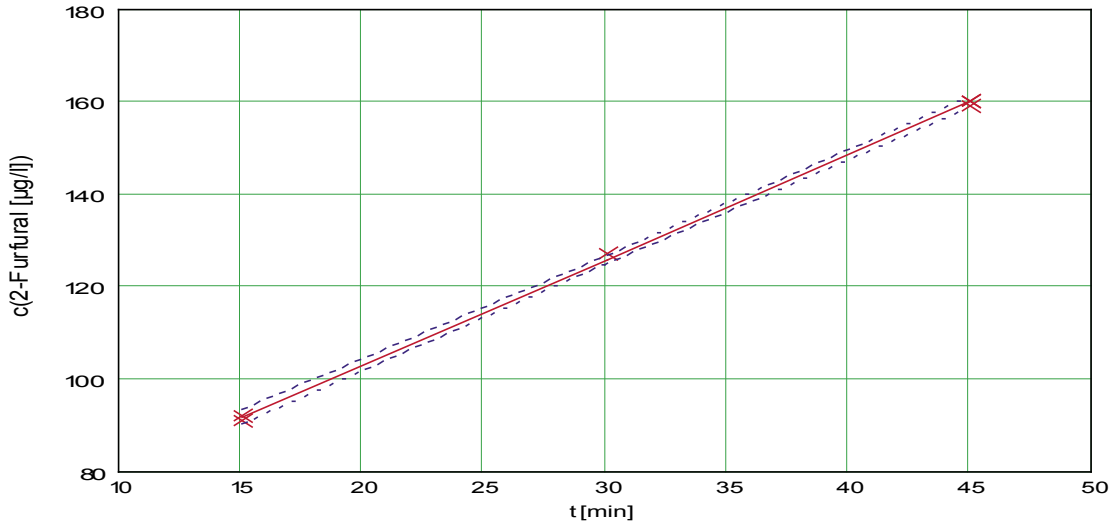

Fig. 11 Increase of the concentration c of 2-Furfural over a time t at 99,4 °C

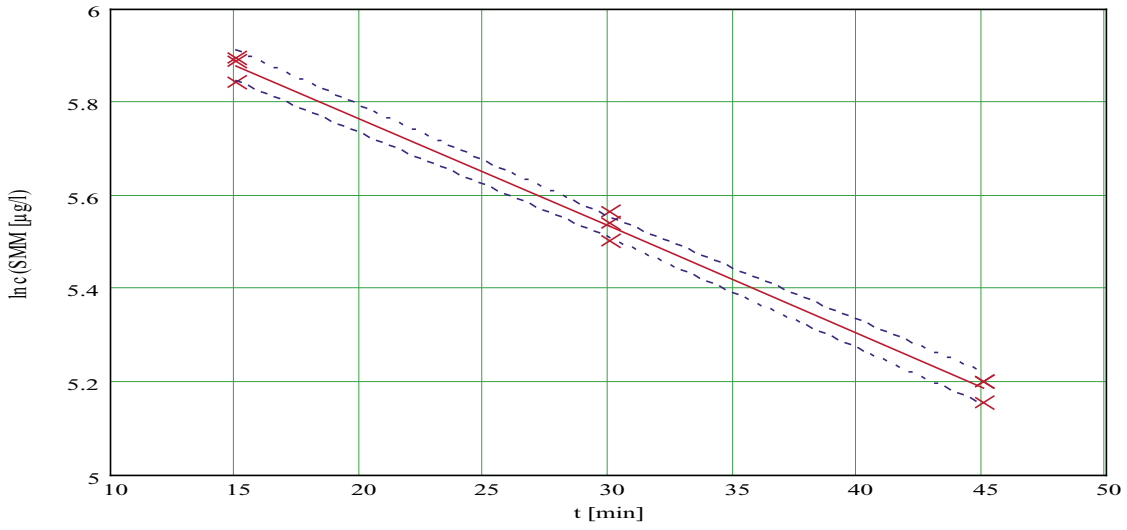

Fig. 12 Decrease of the logarithm of the concentration c of SMM over a time t at 99,4 °C

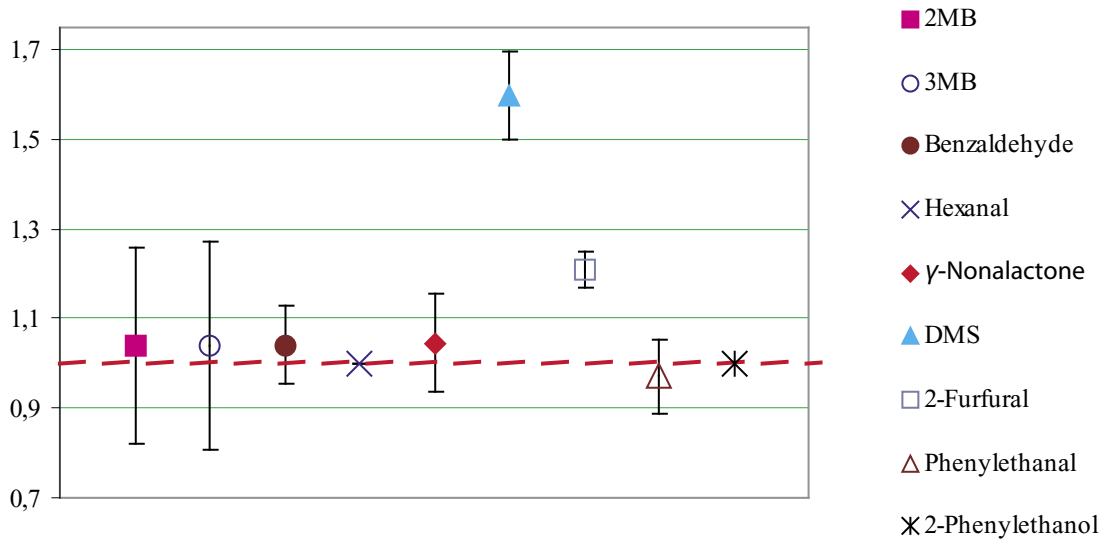

Fig. 13 Increase of aroma compounds during a whirlpool rest of 30 min.