



## Short communication

## Dynamic changes in the volatiles and sensory properties of chilled milk during exposure to light

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## ARTICLE INFO

## Article history:

Received 12 March 2016

Received in revised form

11 July 2016

Accepted 15 July 2016

Available online 21 July 2016

## ABSTRACT

Exposure of milk to light causes photo-oxidation and off-flavour generation. To characterise these reactions, semi-skimmed (1.5% fat) and whole (3.8% fat) extended shelf-life cows' milk were exposed to light for 20–48 h at 4 °C and volatiles in the milk headspace were measured on-line using proton-transfer-reaction mass spectrometry (PTR-MS). The flavour of the whole-milk was assessed by aroma profile analysis on both orthonasal/retronasal odour and taste after 0, 0.25, 1, 6 and 24 h light-exposure. Sensory changes perceived in milk exposed to light for up to 6 h varied in intensity and between replicates, most notably a transient sensory defect being detectable after 0.25 h exposure, but these changes did not correspond to any volatile organic compound (VOC) generation detected by PTR-MS. After 24 h, several compounds showed enhanced release profiles. Principal components analysis related these VOCs to changes in the sensory properties of the milk, described as *oxidised/rancid/hay-like*.

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## 1. Introduction

Exposure of milk to natural or artificial light can cause, within 15 min, the development of off-odour/flavours characterised as being *burnt protein*, *oxidised*, *cabbage* and/or *mushroom-like* (Duncan & Webster, 2010; Stull, 1953). As exposure time to light increases, the intensity of the aforementioned initial “sunlight” or “activated” flavour can decrease, before new off-flavours described as *cardboard-like*, *metallic* or *rancid* become dominant (Hedegaard et al., 2006; Jung, Yoon, Lee, & Min, 1998; Stull, 1953). The initial odour defects are attributed to the light-activated oxidation of protein and amino acids, such as methionine, into a cascade of volatile organic compounds (VOCs), often reported to include methional, methanethiol, hydrogen sulphide, dimethyl sulphide and dimethyl disulphide (Samuelsson, 1962). The scientific literature is not fully in agreement on the chemical identity of the compounds detected or their relative abundances. Differences between studies are often reported, but these are not unexpected as the VOCs detected in any single study will depend on a wide

range of factors. These include the intensity, wavelength of light and duration of light exposure, milk composition (fat level, fatty acid composition), the concentration of photo-sensitisers (riboflavin, protoporphyrin, chlorophyll) or quenchers/antioxidants (ascorbic acid, beta-carotene, tocopherols), the photoreaction type (I or II) that occurs, packaging material, the stability of compounds formed, and lastly the accuracy of the analytical method employed (Hedegaard et al., 2006; Min & Boff, 2002; Whited, Hammond, Chapman, & Boor, 2002; Wold, Skaret, & Dalsgaard, 2015).

In contrast, the mechanisms of formation and the compounds responsible for the *cardboard-like*, *metallic* and *rancid* flavours that dominate after longer (>12 h) periods of light exposure appear to be mostly well-understood, being universally attributed to the formation of secondary lipid oxidation products, including carbonyl compounds (aldehydes and ketones), alcohols and hydrocarbons (Hedegaard et al., 2006) and to an increase in volatile sulphur-containing compounds, such as dimethyl disulphide (Jung et al., 1998).

Recently, the dynamic temporal nature of the changes in VOCs occurring in light-exposed extended shelf-life (ESL) milk was investigated using proton-transfer-reaction mass spectrometry (PTR-MS) (Beauchamp, Zardin, Silcock, & Bremer, 2014). The

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concentrations of VOCs such as methanethiol and acetone/propanal increased within minutes of exposing the milk to light at room temperature (27 °C), reaching a peak after as little as two and four hours, respectively. Other compounds such as heptanal, hexanal, dimethyl sulphide and benzaldehyde started to steadily increase after approximately four to six hours.

To gain a better understanding of the relationship between VOC generation and sensory changes during light exposure, the present study involved dynamic, on-line headspace analyses by PTR-MS of milk samples exposed to light for up to 48 h at 4 °C. The VOC profiles recorded were compared with the sensory attributes obtained from a trained panel that assessed the flavour of the milk after light exposure lasting 0, 0.25, 1, 6 and 24 h, respectively.

## 2. Materials and methods

Semi-skimmed (1.5% fat) and whole (3.8% fat) extended shelf-life (ESL) bovine milk (500 mL Tetrapak™ cartons, Molkerei Weihe, Freising, Germany) were obtained from a local supermarket and held at  $4.5 \pm 0.5$  °C prior to and during light exposure. Milk (400 mL) was transferred into 500 mL transparent glass bottles (Schott AG, Mainz, Germany) and the headspace volume (approximately 150 mL) above the milk was purged and dynamically sampled via glass tube connections in the lid. Until exposure to light, the bottles were wrapped in aluminium foil and milk samples were poured into the bottles under darkened laboratory conditions. Control (no light exposure) samples were kept foil-wrapped throughout the duration of the experiment. A polytetrafluoroethylene (PTFE) coated magnetic stir-bar (100 rpm) stirred the milk throughout the measurements. The integral irradiance intensity of the four fluorescent tubes (TL-D 15W/840, Philips), positioned 20 cm from the milk, was  $10.6 \text{ W m}^{-2}$ . The spectral emission of the fluorescent tubes encompassed wavelengths between 405 and 640 nm, with peaks of maximum emission at 430, 405 and 610 nm. The experimental set-up is shown in schematic form in Beauchamp et al. (2014). Two experiments were carried out for each milk type. For semi-skimmed milk, both experiments lasted for 20 h, whereas for the whole-milk samples one experiment was run for 20 and one for 48 h.

VOCs in the headspace of the milk samples were measured continuously using a high-sensitivity PTR-MS (IONICON Analytik GmbH, Innsbruck, Austria) at an E/N of 132 Td operating in mass scan mode. VOCs that clearly exhibited changes as a result of light exposure were tentatively identified based on published reports of compounds in photo-oxidised milk, their typical fragmentation patterns in PTR-MS (associated  $m/z$ ), and by the relative intensities of their natural  $^{13}\text{C}$  and  $^{34}\text{S}$  isotopologues in comparison with the expected (theoretical) values, as described by Beauchamp et al. (2014).

Sensory analyses were carried out on the whole-milk samples by a panel (5 males, 4 females, aged 25–50 years) trained in recognising well-known odour-active oxidation markers in milk. Prior to each assessment, the panellists were primed on the recognition of typical milk odour attributes by using reference compounds. It should be noted that, due to the requirements of the different experimental approaches, the VOC analysis by PTR-MS was carried out on different batches of milk than the sensory evaluations. Milk samples were evaluated both orthonasally and retronasally by aroma profile analysis (APA) carried out in two sessions with five samples each. Unexposed (reference) and light-exposed milk samples at exposure times of 0.25, 1, 6, and 24 h were ready for sensory analysis at the same time. Orthonasal and retronasal attributes, as well as taste descriptors, of each milk sample were collected and the panellists were asked to score the

intensities of these attributes on a seven-point scale from 0 (no perception) to 3 (strong perception) at intervals of 0.5. APA was performed in a sensory room at  $21 \pm 1$  °C. The samples (20 mL) were presented in lidded glasses (140 mL) labelled with an arbitrary three-digit code and presented in a randomised order. Principal components analysis (PCA) was performed using the Unscrambler software.

## 3. Results and discussion

Upon exposure to light, the increase in the concentration of methanethiol ( $m/z$  49) was very rapid in both milk types (Fig. 1A and B). Methanethiol has been proposed to either be a degradation product from methional or to be formed directly from degradation of methionine, and is believed to contribute to the early *burnt*, *oxidised*, *cabbage-like* off-flavour of photo-oxidised milk. As methional itself is generated by the oxidation of methionine, these data demonstrate not only the speed of these reactions but also their variability; duplicate samples using milk samples from the same batch displayed striking variations in both intensity and duration of the methanethiol signal.

The disappearance of methanethiol is due to its oxidation into dimethyl disulphide (DMDS), which may potentially be further oxidised to the odourless, non-volatile methane sulphonic acid (Barnes, Becker, & Mihalopoulos, 1994). A slight increase and then decrease in DMDS ( $m/z$  95) appears to occur as the methanethiol peaks disappear (Fig. 1, replicate 2, and Fig. 1, replicate 1). The fact that there was no visible change in the DMDS peak in the replicate sample with the smaller methanethiol peak (Fig. 1, replicate 1, and Fig. 1, replicate 2) supports the observation that the release of these two compounds is related. The later increase in DMDS level is likely due to a decrease in the rate of oxidation of DMDS. All other VOCs assessed for both milk types showed good reproducibility between replicates and the PTR-MS performance was constant, as indicated by a consistent reagent ion signal and stable instrumental parameters. As such, it seems likely that the differences seen in the concentration of methanethiol between replicates is not due to either minor variations in the PTR-MS performance or in the composition of the milk within a batch, but rather to differences in the rate of the two reactions that lead to the generation and then breakdown of this compound.

The concentrations of aldehydes such as formaldehyde ( $m/z$  31), acetaldehyde ( $m/z$  45), isoprene/pentanal ( $m/z$  69), hexanal ( $m/z$  83), heptanal ( $m/z$  97; data not shown) increased over time (Fig. 2), as did the concentration of DMDS (Fig. 1) and diacetyl (data not shown). Hexanal is the main oxidation product from the oxidation of n-6 polyunsaturated fatty acids, such as linoleic acid, commonly found in milk. Along with pentanal and DMDS, it is associated with the *cardboard-like* or *metallic-like* off-flavours reported in milk after prolonged exposure to light (Hedegaard et al., 2006; Jung et al., 1998; Stull, 1953).

Over the first 24 h of light exposure, the rate of increase and concentration for all compounds measured, with the exception of DMDS, were the same for both the semi-skimmed and whole-milk samples. Presumably, in whole-milk, due to its higher lipid concentration, the reactions would proceed for longer, ultimately leading to a higher concentration. Differences detected in DMDS are presumably also related to differences in its rate of formation and degradation, as discussed above.

The sensory data from the APA assessments on the light-exposed milks were analysed by PCA conducted on score loadings of 18 attributes (five orthonasal and ten retronasal odours, one texture and two taste attributes) that significantly discriminated among the samples (Fig. 3). Taking the 0 h milk as reference

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