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Food monitoring based on diode laser gas spectroscopy

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Abstract Food is frequently packed in a controlled environment of gas, in order to extend shelf life. It is of great importance to be able to monitor the status of the packed food to ensure quality. We demonstrate a technique to monitor the gas inside packages non-intrusively by using a laser spectroscopic method in scattering solid materials. The technique named GASMAS (GAs in Scattering Media Absorption Spectroscopy) is based on tunable diode laser absorption spectroscopy and relies on the fact that free gas inside solid materials absorbs much sharper spectrally than the bulk material. Results from time dependent measurements of molecular oxygen and water vapour in packages of minced meat, bake-off bread, and the headspace of a milk carton are presented. We show that the technique allows gas measurements inside the food through the package, and assessment of the integrity of the package.

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1 Introduction

Food handling, preservation and packaging is an important aspect of great public interest and concern. The natural presence of oxygen in food products and packaging environments, hastens chemical breakdown and microbial spoilage of the food products. Traditional packaging methods are therefore largely being replaced by newer techniques, frequently falling under the Modified Atmosphere Packaging (MAP) or Controlled Atmosphere Packaging (CAP) categories. These methods replace the natural oxygen content inside the package with other gases such as carbon dioxide (CO_2) or nitrogen (N_2). Food decay and fouling are largely the result of oxidative processes on the one hand, and microbial action on the other hand. Such deteriorating processes are further accelerated with an increased storage temperature. Foods are frequently packed in plastic films, mostly made of polyethylene (PE), polyethylene terephtalate (PET), polyvinyl chloride (PVC), polypropylene (PP), or mixtures thereof. Films may be completely tight or being semi-permeable. An equilibrium of gas concentrations may arise due to the interaction with the product and the gas contained in the package. Here, different permeability of the film to different gases is an important aspect. Frequently, the gas composition is actively changed at the time of packaging, either by flowing gas during the packaging or by first subjecting the product to vacuum followed by inlet of the desired gas mixture [1–4].

Oxygen is a very active gas and it is therefore important to control its concentration in food packaging. Generally, it is desirable to reduce its concentration from ambient (21 percent) to a few percent, reducing the oxidative processes and thereby extending the shelf life. Reducing the oxygen concentration even further can lead to the onset of fermentation, which is unwanted in, e.g. fruit storage [5].

However, other products, such as bakery, poultry and bacon, can advantageously be stored in an oxygen-free surrounding. There is one instance when an oxygen concentration above the ambient (even up to 80%) is applicable; for the treatment of meat to keep the red pigment of myoglobin that gets reduced to deoxymyoglobin in anoxic environments, resulting in brown or greyish meat colours [6].

Carbon dioxide is an effective replacement to oxygen as an anti-microbiological gas. High concentrations of this gas prevent the growth of aerobic bacteria. In addition, low temperatures are good to prevent such growth, also because water and lipids dissolve carbon dioxide much better at low temperatures. Nitrogen behaves like an inert gas in food packaging. It does not dissolve well in water or lipids and thus ensures that a package looks filled and is not collapsing. Pasta is often packed in 100% nitrogen. Frequently, a combination of high carbon dioxide and nitrogen concentrations is used in MAP, e.g. in cheese and cured-meat packaging.

The packaging obviously also prevents a product from drying out and it protects the product from external microbial attack. *Aeromonas hydrophila*, *Clostridium botulinum*, *Yersina enterocolitica*, *Listeria spp.*, and *Escherichia coli* are examples of pathogens which grow even under refrigerated conditions [4].

It is of great importance to be able to assess the status of packed food to ensure its quality and suitability for consumption. Many sensing techniques have been developed. However, some spoilage micro-organisms do not cause overt evidence of spoilage [4, 7]. Gas chromatography and other sampling techniques require puncturing the package for gas extraction. Measurement techniques should preferably be non-intrusive in nature, in order to maintain packaging integrity and reduce waste of samples. In particular, not breaking the package is a matter of considerable importance in the MAP community. Measurement of the oxygen contents in a sealed package can be done by performing optical measurements. This can be done using small sensor disks prepared to change in colour in the presence of oxygen. Alternatively, and more commonly used, the sensor disk is prepared with a ruthenium- or platinum-containing dye, the fluorescence of which is quenched by oxygen [8]. However, the techniques are intrusive from the point of view that the small disks have to be introduced in the package at the time of sealing. There is a cost and a safety aspect ensuring that the active reactive agent does not influence the product or the consumer.

Gas absorption spectroscopy in a spectral region where the packaging material as well as the product is transparent is of particular interest to ensure non-intrusive, real-time measurements. This is the route we have taken, and below we will report our initial experience on gas monitoring in packages of meat, bakery products and milk.

Natural products, such as foods, frequently exhibit a very strong light scattering, making the application of normal gas spectroscopic techniques [9] difficult. Normally, gas monitoring, whether pursued with classical or optical techniques, is limited to the headspace in transparent packages. Recently (in 2001), a method for gas analysis in scattering materials was introduced in our group. The GASMAS (GAs in Scattering Media Absorption Spectroscopy) technique analyses the sharp absorptive imprint in the scattered light leaving the organic material [10–12]. This means that the gas inside the product in the form of pores can be analysed optically for the first time non-invasively. The pores can be small compartments or a larger cell surrounded by scattering material. Mostly, molecular oxygen gas has been explored using semiconductor lasers operating around 760 nm, but also water vapour has been studied [12]. Examples of previously studied samples with the GASMAS technique are polystyrene foam, fruit, wood, and human sinuses [11–15]. The possibility to measure two gases simultaneously is a particular asset when using GASMAS, since the multiple scattering in porous/inhomogeneous media makes the optical path length undefined, complicating the straightforward application of the Beer–Lambert law for concentration evaluation. Water vapour (interrogated around 935 nm) can be used as a reference gas. Under the condition of a 100% saturation, which is the case in an enclosed volume with liquid water present, the concentration of water vapour is known, since it is only determined by the temperature. In this way the concentration of, e.g. oxygen can be determined by normalisation, assuming that the optical properties are close to similar for the two wavelengths employed, or that proper correction can be applied. This normalisation procedure has been used in connection with diagnostic gas monitoring for human sinuses and is discussed in [13] and [15].

In the food-related area, we have performed initial oxygen measurements on fruits, especially apples [14]. We have now extended these types of measurements to minced meat, bakery products and an intact gable top carton with milk.

In the next section we describe the experimental setup used for the measurements which are described in a subsequent section. The data analysis employed is then explained. Finally, the results are discussed and an outlook for the future is made.

2 Method

2.1 Experimental setup

An overview of the spectroscopic equipment used to monitor gases in food products in packages is given in Fig. 1. The setup is basically the same as developed for human sinus cavity monitoring, and a detailed description can be found in [15].

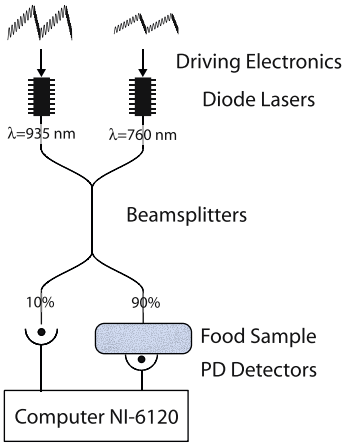

Fig. 1 Experimental arrangement for simultaneous measurements of free molecular oxygen gas and water vapour

The wavelength of two pigtailed distributed feedback (DFB) lasers (Nanoplus) are scanned across the R11R11 absorption line of molecular oxygen at a vacuum wavelength of 760.564 nm, and the rotation-vibrational transition (vibration; (000) → (121), rotation; $J'' = 3 \rightarrow J' = 4$, $K_a'' = 0 \rightarrow K_a' = 0$, $K_c'' = 3 \rightarrow K_c' = 4$) of water vapour at 935.686 nm, by employing sawtooth ramps at 5 Hz on the injection currents. At these wavelengths the food stuffs and the packages are transparent, enabling gas detection non-intrusively. Sinusoidal modulations of 10295 Hz for molecular oxygen and 9015 Hz for water vapour are superimposed on the sawtooth ramps to enable phase sensitive detection. The laser light is fibre-optically coupled together and divided into two arms, the reference arm and the sample arm. The reference arm carries a small fraction of the laser light and is directly guided to a photo diode (S3590-01, Hamamatsu). The sample arm contains a large portion of the laser light and is guided to the food sample. The diffusely emerging light of the food package is detected with a large area, 18 × 18 mm, photo diode (S3204-08, Hamamatsu). The current signals from the detectors are amplified in two steps, first with a trans-impedance amplifier (DHPCA-100 and DHPCA-200, Femto Messtechnique GmbH) and then with Stanford Research Model SR560 units which also function as a high-pass filter (12 dB/octave at 3 kHz), removing the sawtooth part of the signals. The high-passed signals are synchronously sampled with a PCI card (National Instrument 6120 with maximum sample rate 800 000 S/s and 16 bits). The sample rate used in the experiments was 400 000 S/s. The collected data are then analysed by a Matlab program performing the digital wavelength modulation procedure enabled by the synchronised sampling.

2.2 Gas investigation

Packages of minced meat, bake-off bread, and milk in a gable top carton were investigated using the technique described.

To study the possibility to monitor changes in a modified atmosphere the gas composition was measured for one minced meat tray package over three days. The meat packages were purchased in a local grocery store, which had packed the minced meat in a tray of polystyrene foam, and covered it by a plastic film. The fibre-coupled light was injected through the plastic film covering the minced meat and the light passing through the meat and tray was detected. To reduce the data analysis process and due to previous experience of slow time dependencies an average time of 10 minutes was used despite that an average time of 1 minute was sufficient regarding photon statistic. Previous to the measurements the package was placed in a cold environment. However, the measurements were performed in surrounding room temperature, resulting in different temperatures of the sample over time. The temperature was monitored with a temperature logger (Picotechnology TH-03). Two temperature sensors were used. One was placed on top of the plastic film of the studied minced meat sample and one was inserted into the contents of a similar package as the one under-going the spectroscopic study. The temperature values were also averaged for 10 minutes.

For the bake-off bread a plastic package containing eight buns packed in a modified oxygen-free atmosphere was used. The light was injected through the plastic film into one bun. The light was detected in a transmission mode. After one hour a large sized hole of about 1 cm in diameter was made in the package, resulting in air flowing into the package. The signal was measured for 24 further hours. An average time of 10 minutes was used to reduce the data evaluation process. The package was all the time at room temperature.

The headspace of a milk container was monitored by injecting the light through one surface and detecting scattered light through a different surface as shown in Fig. 2. The milk carton is made of white and red paper, about 0.5 mm thick. An averaging time of 1 minute was used. After around 30 minutes a small hole of about 2 mm diameter was introduced.

2.3 Data analysis

From the data collected with the PCI card, each laser, and hence the different gases, can be distinguished due to the different sinusoidal modulation frequencies. The synchronised sampled data enable post analysed phase-sensitive detection. Here this is done by using fast Fourier transformation. A detailed description of the technique is found

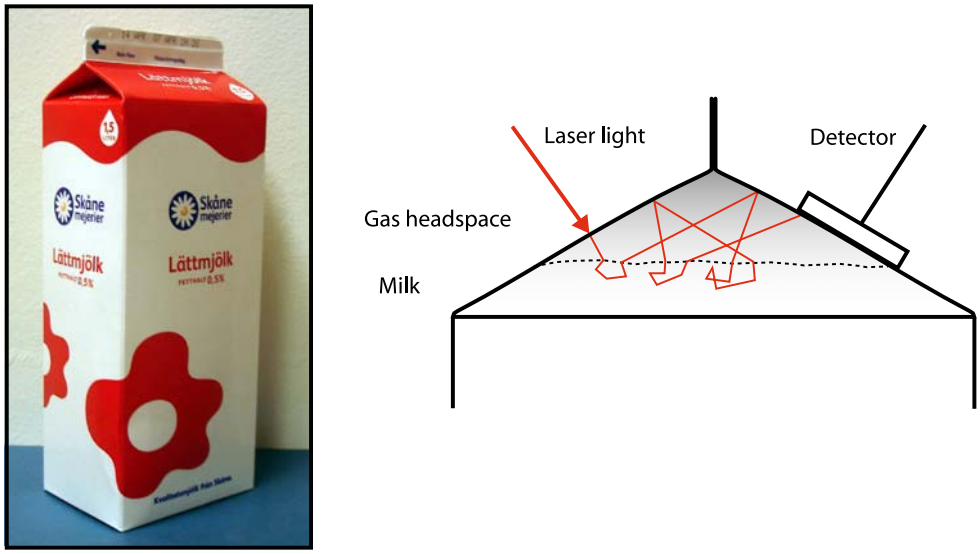

Fig. 2 (**a**) Photograph of a milk carton. (**b**) Milk carton measurement geometry, one possible light path illustrated

in [16]. Briefly, the collected data are Fourier transformed. A window function selects the desired harmonic and down-converts it to zero frequency, before inverse Fourier transformation is made. The absolute value of the complex signal after phase adjustment results in the wavelength modulation spectroscopy (WMS) signal.

The 2f WMS signal is normalised by division with the offset of the 1f WMS signal, since this offset for given laser driving conditions is proportional to the light intensity. To correctly utilise such normalisation for quantitative gas analysis, it is necessary that calibration measurements on gas with known concentrations are performed for identical laser driving conditions. The normalised 2f WMS signal is then subjected to balanced detection. This process is made to subtract interference phenomena that occur in the setup, and other systematic defects. The balanced detection is made by minimising the difference between the normalised 2f WMS signal, $y_{\text{samp}}(x)$, and a function containing both a polynomial $p(x)$, a polynomial $q(x)$ times the reference 2f WMS signal $y_{\text{ref}}(x)$, and an ideal signal shape $y_{\text{ideal}}(x)$ (the 2f WMS signal obtained for a measured long air path). The variable x refers to sample point of the data:

$$y_{\text{samp}}(x) = p_0 + p_1 x + p_2 x^2 + (q_0 + q_1 x) y_{\text{ref}}(x) + c \cdot y_{\text{ideal}}(x - x_0). \quad (1)$$

The shift of the ideal signal centered at x_0 is present to account for small drifts. The amplitude of the fitted ideal signal is proportional to the absorption of the species- and the path length the photons have traveled in the sample. As a calibration the standard-addition method is used, by converting the amplitude to an equivalent mean path length L_{eq}. This property is the length the light has to travel through ambient air (at 24°C and a relative humidity of 20%) to obtain the same signal, and is dependent of both the absorption of the gas and the traveled path length in the gas of the sample. We note that it is important to measure temperature and relative humidity accurately, since errors directly transfer into the evaluated oxygen concentration.

Due to the complex dependence of L_{eq} on the bulk properties, it is of interest to divide it with the L_{eq} of another species of known concentration for which the interrogated light has traveled the same path length. Under the assumption that scattering and absorption of the bulk material of the sample are equal for the two wavelengths used for measurement on the two gases, the path lengths are equal. If liquid water is present in a sample with closed volume, then the concentration of water vapour can be determined if the temperature is known.

3 Results and discussion

3.1 Minced meat

Typical molecular oxygen and water vapour signals obtained in measurements of minced meat are shown in Fig. 3. The grey line is an ideal signal fitted according to (1).

Figure 4a shows the obtained L_{eq} values of water vapour in a minced meat package over time. The temperature measured inside a similar package is shown in Fig. 4b. The corresponding partial pressure is calculated through the Arden Buck equation [17] and presented in Fig. 4c. The temperature measured on top of the minced meat sample correlated with the one measured inside the meat, only with an offset as a difference. The sharp increase of signal can be seen to originate from the temperature dependence of the water vapour signal. To eliminate the temperature effect the ratio

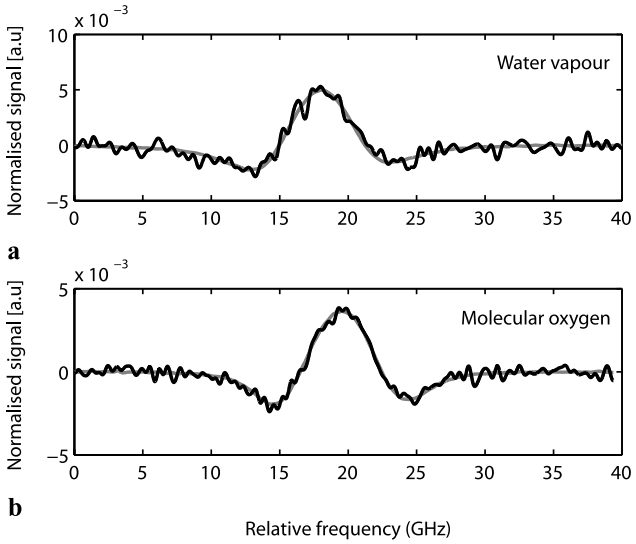

Fig. 3 Signal obtained in measurements of a package of minced meat in transmission mode. The *grey line* indicates the fit of an ideal signal according to (1). (**a**) Water vapour signal. (**b**) Molecular oxygen signal

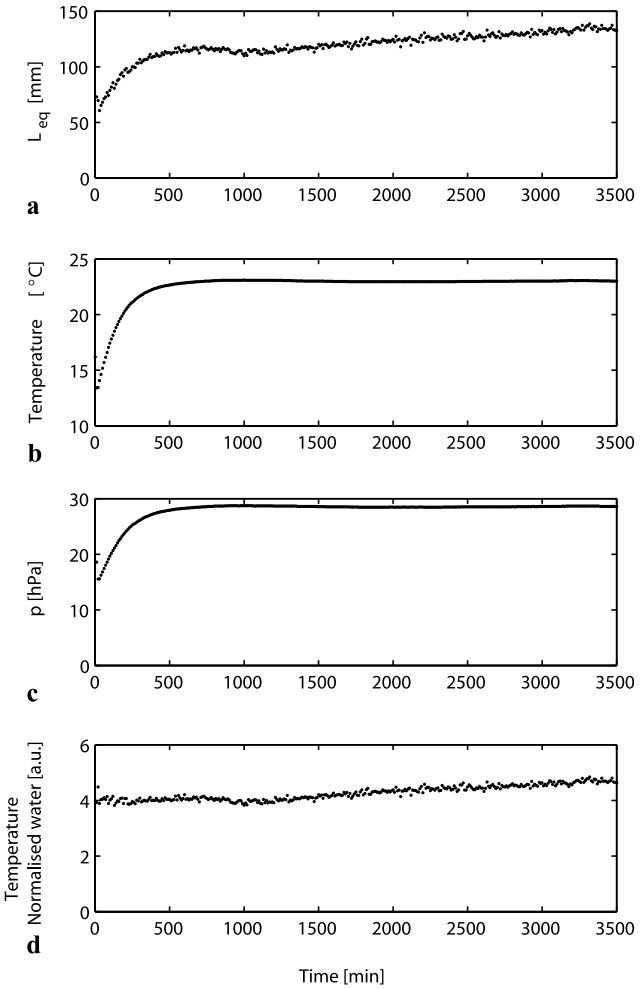

Fig. 4 Measurement of minced meat over time: (**a**) L_{eq} of water vapour, (**b**) temperature measured inside a similar package, (**c**) saturated partial pressure of water vapour corresponding to measured temperature, (**d**) ratio between the L_{eq} of water vapour and the partial pressure of water vapour at different times

of the water vapour signal and the partial pressure of water vapour at the different times was calculated and is shown in Fig. 4d. The normalised water vapour curve increases slightly, which should not correspond to a concentration increase, since a relative humidity of 100% is expected in the closed volume. The change in the temperature normalised water vapour signal could thus be considered to be due to the change in the optical properties in the bulk material or in pore size for the packed minced meat.

The L_{eq} value of molecular oxygen in the minced meat package over time is presented in Fig. 5a. In Fig. 5b, the temperature-compensated water vapour signal, used as a reference to diminish the influence of the sample changes, is shown. The ratios of the L_{eq} values of molecular oxygen and the temperature-compensated water vapour values are presented in Fig. 5c. Division with reference gas measurement results in values not including the scattering and absorption properties of the bulk material, under the assumption that the optical properties in the bulk material are the same for the two wavelengths used. The calculated ratio corresponds to the molecular oxygen in the package, and can be seen to decrease over time, interpreted as the minced meat consuming ambient oxygen by oxidation.

3.2 Bake-off bread

Data for the bake-off bread are shown in Fig. 6. At the dashed line a hole of about 1 cm is made in the package, providing ambient air to freely pass into the package. The initial values of molecular oxygen signal, close to zero, show an absence of oxygen which indicated that the package is tight to oxygen prior to penetration. At puncture, an immediate change is measured in the molecular oxygen and water vapour content. This can be interpreted as the bake-off bread trying to reach a new equilibrium in the new ambient situation. The increase of the water vapour signal shows that a 100% relative humidity was not present in the non-perforated package due to lack of water, not allowing saturation. However, water vapour was present in the non-perforated package since an initial value of 450 mm was measured. The time constant of the diffusion of molecular oxygen and water vapour into the bread bun was $\tau = 211$ min and $\tau = 258$ min, respectively, using an exponential fit.

3.3 Milk carton headspace

Headspace measurements through a scattering package were performed by studying the gable top of a milk carton. Typical signals from the milk carton measurements are shown

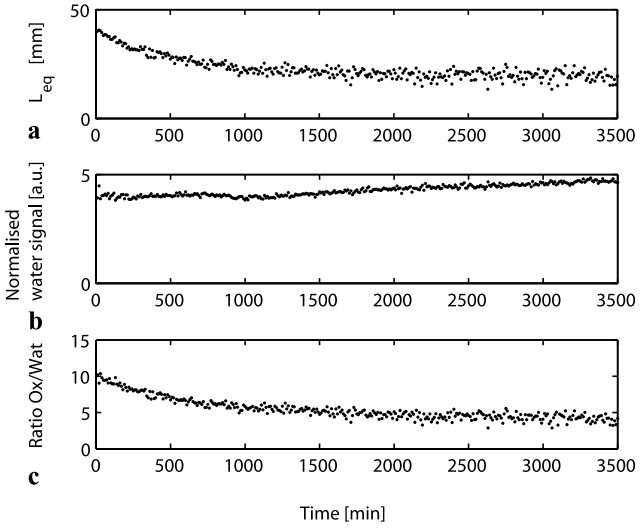

Fig. 5 Measurement of minced meat over time: (**a**) L_{eq} values of molecular oxygen, (**b**) temperature normalised water vapour signal, (**c**) ratio of L_{eq} of oxygen and the temperature-compensated water vapour signal

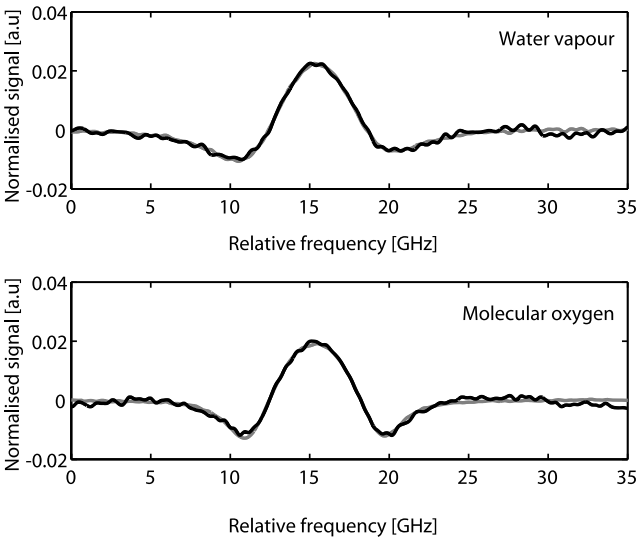

Fig. 7 Signals from measurement on the headspace of a milk carton, with fitted ideal *curves* (*grey*). The accumulation time was 60 s

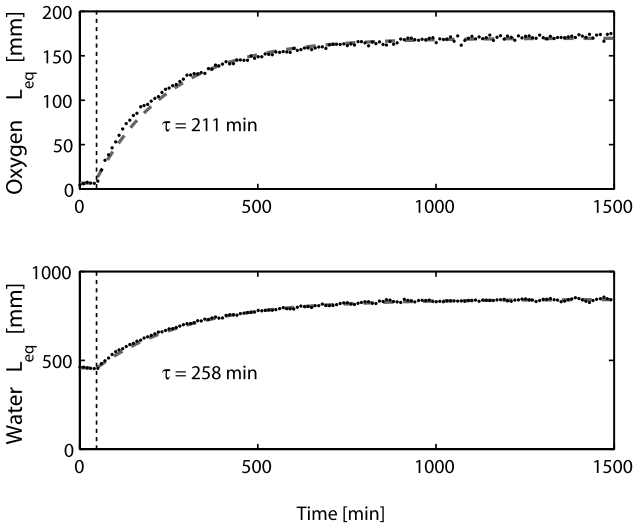

Fig. 6 A bake-off bun inside a modified atmosphere. The *vertical dashed line* indicates when a hole was made in the package. The *grey dashed lines* are exponential fits to the data resulting in the indicated time constants τ

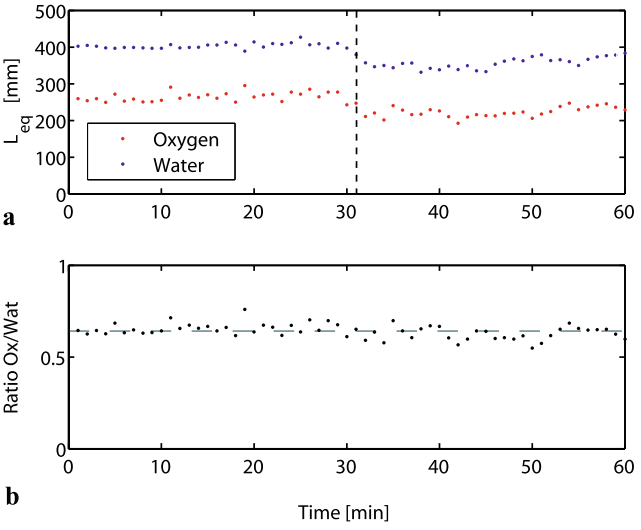

Fig. 8 Data obtained for the headspace of a milk carton. For each data point an accumulation time of 60 s was used. At time around 30 minutes a small hole was punctured at the top of the package. The *grey dashed line* is drawn for the guidance of the eye

in Fig. 7 and correspond to an L_{eq} of 220 mm of molecular oxygen and an L_{eq} of 380 mm of water vapour. Multiple passages over the headspace due to the scattering package and milk indicated in Fig. 2 result in a larger signal than corresponding to the physical geometry. Data for water vapour and molecular oxygen from the measurements over time are shown in Fig. 8a. As the package is perforated an offset in the water vapour and oxygen signal is seen. Under the perforating process small displacements of the detector and injecting fibre are noted, which can provide an explanation for the offset. Small displacements of especially the injecting fibre can give effects on the path length of the detected light. In Fig. 8b, the ratio of the oxygen and water vapour signal is presented and is stable over the whole investigation. A 100% relative humidity is expected since the large wet surface fully moisturises the gas in the head space in spite of the ventilation. This behaviour has also been observed for human sinus cavities [13]. The stable ratio suggests that the oxygen concentration in the headspace in the milk carton is the same as in the ambient air. It can be noted that the variations seen in the stable part of the measurement are not

diminished with the normalisation process with a reference gas. Slow varying residual interference effects are possible explanations to this phenomenon which demands further examination.

4 Conclusions

We present results from measurements showing the feasibility of the GASMAS technique as a powerful tool for studying food stuffs and food packaging. Measurements on minced meat packages, bake-off bread packages and the headspace in a milk carton illustrate the possibility to monitor the packed food stuff, as well as the package integrity, non-intrusively. The stable or only small increase in the temperature-compensated water vapour signal in the minced-meat measurement suggests that in minced-meat monitoring the reference gas might not be necessary in an industrial monitoring device. The increase of water vapour signal as the bake-off bread package is penetrated reflects that a 100% relative humidity was not reached in the non-punctured package. The concentration of water vapour can thus not be calculated and not used as a reference gas. The non-response for puncture of the ratio in the milk carton measurement indicates that the oxygen concentration in the headspace is the same as in the ambient air. The change in the optical path length due to the small displacement in the perforating process was shown to be eliminated by using water vapour as a reference gas. This supports the use of a known water vapour concentration for extracting the oxygen concentration. The oxygen signal referenced to a temperature-compensated water vapour signal is then related to the oxygen concentration, and might be used for non-intrusive checking of fouling. The assumption that the sampled volume of the two wavelengths used is similar has been discussed in [13] where the validity for the case of human sinus monitoring was experimentally noted. At any rate, a correction factor could be determined by independent gas concentration measurement. These aspects will be further explored.

The measurements of the bake-off bread are promising in the way that they indicate that the GASMAS technique is suitable for non-intrusive monitoring of the tightness of the food package. After these proof-of-principle measurements we now aim at in-depth studies of different products in close cooperation with expertise in the corresponding fields.

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