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Non-intrusive Measurements of Headspace Gas Composition in Liquid Food Packages Made of Translucent Materials

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SUMMARY

The increase in chilled food consumption requires enhanced food safety and quality assurance. Food deteriorating processes are affected by the presence of oxygen, combined with factors such as time and temperature. To slow down deterioration processes and prolong shelf life, traditional packaging methods are being replaced by modified atmosphere packaging, for example. Oxygen, which is naturally present in the headspace of most food packages, is then reduced and controlled. Many sensing techniques for food quality assurance have been developed; however, almost all are intrusive, increasing the complication level and causing sample waste. The purpose of this paper is to introduce a non-intrusive technique [gas in scattering media absorption spectroscopy (GASMAS)] for measuring gas composition in the headspace of liquid food packages. The GASMAS method uses diode laser absorption spectroscopy combined with diffuse light propagation to analyse gas located inside solids and liquids. By illuminating the package from the outside and analysing the scattered light that emerges, the absorption from the gas inside the headspace can be studied. The GASMAS technique was evaluated on a series of carton packages with a high-quality orange juice and a nitrogen headspace. A clear variation in oxygen content was measured for samples with different storage times. The results demonstrate the possibility of using the GASMAS method for non-intrusive quality measurements in food products and packaging. They also indicate the potential for the non-intrusive quality assurance applications without waste of samples. A further development of the technique could include 'in-line' quality control of packed food items throughout the food packaging supply chain. Copyright © 2011 John Wiley & Sons, Ltd.

INTRODUCTION

The preference among consumers in modern society for fresh products means that chilled foods are increasingly competing with their frozen and ambient counterparts. Fresh or chilled food is more sensitive, thus enhancing the demand from food consumers to be able to trust that the food they buy and consume is safe. Important issues in the transfer from ambient or frozen food products to chilled food are thus safety and quality, which are identified as increasing concerns emphasized frequently in industry and media.1

The demand for fresh chilled food has created a need for distribution of fresh products year round. Fresh and chilled foods require both quicker distribution because of shorter shelf life and better product and package integrity because of safety and quality issues at the point of consumption.1 The two most important factors concerning shelf life are time and temperature. Most of the deteriorating changes that take place in food are temperature dependent and occur at a slower rate at lower temperatures.2 In addition to the time and temperature parameters, the natural presence of oxygen in
food products and packaging environments hastens chemical breakdown and microbiological spoilage of food. Traditional packaging methods are therefore largely being replaced by newer techniques such as modified atmosphere packaging (MAP).⁴ A result of food deteriorating aspects, food handling, preservation and packaging have become important aspects of great public interest and concern. The MAP technology theoretically meets the new consumer requirements of prolonged shelf life for chilled or fresh products, and the MAP packaging concept is growing in importance in the food packaging market. The main benefit of MAP is argued to be the reduction of indirect costs because of less product waste.⁵ But, with the increased quality and safety concerns, the importance of being able to assess the status of packed food to ensure its quality and suitability for consumption must also be stressed. Many sensing techniques have been developed; however, most of them destroy the packaged sample, thus causing waste of both products and packages. For example, gas chromatography and other sampling techniques require puncturing the package for gas extraction, whereas measurement techniques should preferably be non-intrusive in nature, in order to maintain packaging integrity and reduce waste of samples.

This paper demonstrates a non-intrusive sampling technique for quality assurance in the liquid food packaging industry. The possibility to assess information about the gas composition non-intrusively has previously been illustrated on a gable top carton package for milk, with a non-modified atmosphere (i.e. air headspace).⁶ We have now applied the method to a series of carton packages for fresh orange juice packed in a modified atmosphere of nitrogen. Three series of high-quality orange juice packaged in flexible cartons under modified N₂ atmosphere and with different storage times have been measured with respect to their gas composition. Results from these measurements are reported and discussed. The potential for the applications of non-intrusive quality assurance in the liquid food packaging industry is also elaborated.

The paper first presents background descriptions of MAP and non-intrusive package measurements. The method used is then described. The initial experience from gas monitoring experiments on milk, bread and meat packages is reviewed, and the results from the present experiments are reported and analysed. The results and implications of using the method are then discussed, and conclusions are presented.

MODIFIED ATMOSPHERE PACKAGING

Oxygen is a very reactive gas, naturally present in air. Most packaged food items come with a natural headspace of air between the product and the package. Oxygen is thus frequently present in the headspace. Because of the high activity of this molecule, it is important to control its concentration in order to secure quality and increase the shelf life of the product. Generally, it is desirable to reduce its concentration from ambient (21%) to a few per cent or to a completely oxygen-free environment. By replacing the oxygen in the headspace, the oxidative processes are reduced and the shelf life of the food product is extended.⁶

In order to reduce the natural concentration of oxygen in air, food products are packaged in modified or controlled atmospheres. MAP, as used in our study, is defined by Hintlian and Hotchkiss as ‘the packaging of perishable product in an atmosphere which has been modified so that its composition is other than air’.⁷ In MAP, the natural oxygen content inside the package is replaced with other gases such as carbon dioxide (CO₂) or nitrogen (N₂). 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 a vacuum followed by the inlet of the desired gas mixture.⁶,⁸–¹⁰

Fresh products such as fruits or cured meat are the most common products to pack in modified atmosphere.⁴ But, more frequently, products such as high-quality fruit juices are packed in modified atmosphere in order to reduce deterioration from oxidation and to extend the product shelf life. The modified atmosphere slows chemical and biochemical deteriorative processes as well as slows or prevents the growth of spoilage organisms.³ For high-quality fruit juices, nitrogen is the most common gas to use in the headspace to replace oxygen. Nitrogen is an inert gas that does not dissolve well in water or lipids and thus ensures that a package looks filled and does not collapse. Nitrogen has no antimicrobial activity, and by displacing oxygen in the headspace of packages, the oxidative processes of the products are delayed.
For MAP, the package integrity and tightness are necessary to maintain the correct composition of gas inside the package, thus securing that no gas exchange takes place between the package and its environment. Berlinet et al.\textsuperscript{11} argues that it is important to control the oxygen permeability in order to secure the prolonged shelf life of liquid food products, such as high-quality orange juice. Packages with a modified atmosphere thus require packaging materials that are tight to gas transfers, in order to avoid oxygen from getting into the headspace. For packages that have an exchange (intended or unintended) with the outside environment, equilibrium will be reached between the inside and outside of the package over time with oxygen entering the headspace. Furthermore, in a modified atmosphere package, equilibrium of gas concentrations inside the package may arise because of the interaction between the product and the gas contained in the package. Measurement of the headspace gas composition assesses the simultaneous gas movement from permeation and through the exchange from product to headspace in a dynamic MAP system.\textsuperscript{12}

**NON-INTRUSIVE GAS SENSING OF FOOD PACKAGES**

The measurement of oxygen contents in sealed packages may be the most pertinent aspect of monitoring the gas composition in the headspace of packages. Oxygen assessment can be carried out by performing optical measurements, using small sensor discs that change colour in the presence of oxygen. Alternatively and more commonly used, the sensor disc is coated with a dye containing ruthenium or platinum, with fluorescence properties that decrease with the amount of oxygen.\textsuperscript{13} However, these techniques are intrusive because the small discs have to be introduced in the package at the time of sealing. In addition, cost and safety aspects need to be considered to ensure that the active reactive agent does not affect the product or the consumer. From a safety and consumer perspective, non-intrusive measurements without devices put on or inside the package are thus called for. All extra items incur extra direct and indirect costs, such as additional handling time and machine investments. Non-intrusive measurements also allow for measurements over time of a package during its entire shelf life.

Gas absorption spectroscopy\textsuperscript{14} is an alternative gas sensing method for food packages. It is of interest because it can provide non-intrusive, real-time measurements without the need to add sensors inside the packages. The technique is based on the fact that each molecule absorbs light in a unique way, making it possible to identify and quantify with absorption spectroscopy. A limitation to its conventional implementation is the need for transparent packaging and headspace. In 2001, an alternative approach to gas absorption spectroscopy called gas in scattering media absorption spectroscopy (GASMAS) was introduced, enabling the sensing of gas surrounded by scattering media.\textsuperscript{15} This technique made it possible to analyse gases inside natural products, such as different kinds of food, or human tissues for medical applications,\textsuperscript{16} where a strong light scattering often makes the application of conventional gas spectroscopic techniques difficult. The principle of GASMAS is that the spectrally sharp gas absorption can be distinguished from the broadband absorption of liquids and solids. This results in a small gas absorption signal (order of 1 in 10 000) being extracted from light passing through a scattering and absorbing material despite transmitting only a minor fraction of the injected light. With the GASMAS method, gas located in cavities inside products, such as different food items (e.g. meat, bread, fruit, liquids), as well as different scattering packaging materials, such as plastic and paper, can be analysed optically for the first time non-invasively.\textsuperscript{5} This means that gas inside the headspace of packages that are non-transparent but translucent (i.e. cannot be seen through by the human eye but which allow light to pass through, although in a diffuse manner) can be analysed.

**EXPERIMENTAL SET-UP AND MEASUREMENTS**

This study is based on the simultaneous monitoring of oxygen and water vapour in the headspace of non-transparent but translucent orange juice packages with a modified atmosphere using the GASMAS technique. Oxygen is of major importance for this study, and water vapour is monitored as
a reference gas to enable oxygen concentration evaluation. Three sample sets of orange juice packages with different expiration dates were analysed. Each set consisted of 20 samples.

Experimental set-up

The gas sensing instrument used is depicted in Figure 1 and consists of two diode lasers (DFB Nanoplus, Gerbrunn, Germany), one monitoring oxygen and one monitoring water vapour inside food packages. The two diode lasers operate at wavelengths of 760 and 935 nm, where the food package and the orange juice are translucent, making the GASMAS technique suitable. The laser light was guided to the sample via optical fibres and a hand-held fibre head. The scattered light emerging from the sample was captured by a hand-held 10×10 mm detector (Hamamatsu S3590-01, Hamamatsu, Japan), and the generated signal was sampled by a computer. Wavelength modulation techniques were used to increase the sensitivity of the instrument by sinusoidally modulating the wavelength at about 10 kHz and by studying the generated harmonics. In this study, the first overtone (1f) illustrated on the monitor in Figure 1 was used for absorption evaluation. A detailed technical description, system performance and data evaluation were presented by Lewander et al. It is important to note that the light transducer and detector were hand held and not entirely fixed. In GASMAS, complete fixation of sample, light delivery and detector often results in detrimental interference noise. Systematic ways of circumventing this includes dithering of laser beam and/or sample.

The gas signal obtained is referenced to a calibration measurement of 1000 mm of air, yielding a measure in the unit of millimetre, referred to as the equivalent path length, $L_{eq}$. This quantity is the distance the light has to travel in ambient air to experience the same gas absorption imprint. The absorption is governed by the Beer–Lambertian law and is dependent on both the species concentration and the distance over which the light interacts with the gas. Because the GASMAS technique studies scattered light, the gas interaction distance is unknown, making it necessary to reference the absorption to a calibration measurement. The quantity obtained, $L_{eq}$, is thus dependent on both the optical path length and the gas concentration. This means, for example, that a signal of 20% oxygen with an interaction distance of 25 mm or an absorption signal of 10% oxygen with an interaction distance of 50 mm gives the same $L_{eq}$. However, by measuring water vapour, information about the sampling path can be obtained. A closed environment with liquid water was saturated, giving a known water vapour concentration governed only by temperature. Using the equivalent path length, $L_{eq}$, of water vapour as a measure of the interaction distance also for oxygen resulted in the ratio of the oxygen and water vapour signals being proportional to the oxygen concentration. We rely here on the assumption that 760 and 935 nm laser light probe the same volume.

Earlier measurement experience of food packages

Monitoring of gas inside packages has previously been demonstrated with the GASMAS technique on bake-off bread, packed minced meat and a gable top carton of milk. These early measurements were...
performed on single packages in order to illustrate the possibility to assess information about the gas inside sealed packages non-intrusively. The bake-off bread and the meat package were transparent or partly transparent and had a modified CO₂ atmosphere and non-modified atmosphere, respectively. Measurements were made non-intrusively through the product inside the package. The results illustrated that it was possible to access information about the gas composition sealed inside a packaged product.

The milk studied was packed in a non-transparent gable top carton with non-modified atmosphere (i.e. a headspace of air). The results demonstrated that it was possible to study the absorption of gas inside a headspace non-intrusively even though the package appears to be non-transparent. Both oxygen and water vapour were studied. When the package was perforated, the ratio of oxygen and water vapour absorption signal remained constant. This demonstrates that the headspace oxygen concentration was originally the same as the ambient air. However, an increase in absorption was observed both in the oxygen and water vapour absorption signals following perforation. This phenomenon is interpreted as an effective path length increase because of the movement of the sample when the perforation was performed. The observation illustrated the need to use simultaneous monitoring of water vapour as a reference in these types of measurements.

**Measurement of orange juice packages**

To further analyse the potential of the GASMAS technique as a food packaging quality control tool, a study on larger sample sets with non-transparent packages was performed to obtain statistical data. The study also included exploration of the ability to extract oxygen concentration information in packages with a modified atmosphere headspace.

Three sets of 20 packages of high-quality orange juice, packaged in flexible carton portion packages of 250 ml, with a plastic polyethylene (PE) top and a screw cap opening, were used for measurements (see Figure 2a).

The package consists of a carton-based sleeve made of printable paper coated with layers of PE and with an injection moulded plastic top of PE. The headspace of the package is modified with nitrogen, N₂, to prolong the shelf life of the juice.

The purpose of the experiment was to identify differences in the gas composition between the three sets with different shelf life. The sets were measured on 26 January 2010 and had different expiration dates:

- Set 1: 30 October 2008
- Set 2: 22 August 2009
- Set 3: 23 February 2010

Figure 2. (a) Photograph of a sample of the orange juice packages studied. (b) Illustration of the detection geometry. The light is injected on the side of the plastic top oblate (screw cap taken off) and detected at the top of the package with the cap removed.
The laser fibre transducer was hand held on the side, and the light detector was hand held at the top of the plastic upper part of the package (see Figure 2b). The cap was removed, but the package was still intact because of the plastic oblate, the ‘tamper proof’ seal that needs to be taken away before consumption. A black paper tube was placed around the top of the package top to prevent detection of leakage light passing from the fibre tip directly to the detector. Each package was measured three times with re-positioning of the laser fibre and detector to verify the reproducibility of the technique. The packages were refrigerated during the storage time but placed at room temperature one night before the experiment started. A uniform and known temperature condition for all packages was desired to ensure the ability to calibrate with water vapour. Each package was weighed in order to identify any differences between samples and sets. To confirm that the gas absorption signal originated from the gas inside the package, and for absolute oxygen concentration calibration, one sample from each set was perforated with circular openings of 3 mm and measured with a flow of nitrogen gas and with ambient air in the headspace.

RESULTS

The perforation measurements on one package of each expiration date set showed that the absorption signal originated solely from the gas inside the headspace of the package. As nitrogen gas was flushed into the headspace, the oxygen absorption signal basically disappeared. Further, the perforation experiment also verified that the headspace consisted of a modified atmosphere. Example signals from one package of the set with an expiration date of 23 February 2010 are presented in Figure 3. The intact package gave an oxygen absorption signal of 34 mm. When puncturing the package, the oxygen absorption signal increased, as ambient air flowed into the package. Filling the headspace with nitrogen gas resulted in no oxygen signal (i.e. a signal lower than the noise background, which for this case was equivalent to an $\text{L}_{\text{eq}}$ of 5 mm).

Similar results were obtained for the two other sets with other expiration dates when perforated (see Figure 4). The oxygen absorption signal increased as the packages were perforated and decreased to the noise level as nitrogen was flushed into the headspace. The oxygen absorption signal level of the intact packages as well as the perforated package varied between the sets. Changes in the gas interaction length, because of, for example, different filling levels, optical properties or measuring geometry, could explain such a variation in oxygen absorption signal. However, when forming the ratio of oxygen and water vapour $\text{L}_{\text{eq}}$, the discrepancies between the three samples remained for the intact packages but equalized when the sample packages were perforated and ambient air filled the headspace. It can thus be claimed that the three studied intact packages with different expiration dates have different amounts of oxygen concentration. As noted, the ratio parameter for the perforated packages with ambient air in the headspace all equalized to a similar value, corresponding to 21% of the oxygen concentration. Our observation suggests that the ratio of oxygen and water $\text{L}_{\text{eq}}$ can be used as an oxygen concentration

![Figure 3. Example signals of oxygen absorption from a package that is first intact (left), then punctured (middle) and lastly flushed with nitrogen (right). The black curve is the measured signal, and the grey curve is a fitted ideal absorption imprint.](image)
measure. Here, we rely on the water vapour signal being a measure of the probed path through the gas that is possible under the condition of saturated humidity. Because only small holes are made in the headspace, the water vapour saturation in the enclosing is pertained.

An increase in water vapour signal was observed as the packages were perforated and is thought to be an effect of changed gas volume in the headspace. As the packages were being perforated, it was noted that the top of the cap went from buckling inwards to becoming flat. The decrease in water vapour absorption signal as nitrogen gas was flushed through the headspace is believed to be an effect of an unsaturated gas volume as a result of the flow of nitrogen. The ratio between the oxygen and water vapour absorption signal as an oxygen concentration measure is not feasible under such artificial conditions.

The discrepancies in oxygen content between the intact packages with different expiration dates were further analysed by studying all 20 samples of each expiration date. The ratio parameter (i.e. the measure of oxygen concentration) was monitored, and the results are presented in Figure 5. No large variation was observed between the samples within one set, whereas a pronounced difference between the sets was obtained. Using the ratio value from the perforated packages as 21% oxygen to calculate the corresponding concentration of the intact packages resulted in oxygen contents between 7 and 15% for the three sets. For the newly purchased packages, where the expiration dates had not passed when the measurements were performed, an oxygen concentration of 10% with a standard variation of 1% between the 20 samples was obtained. For the two expired package sets, a lower and higher oxygen concentration was measured: 7 ± 1% for the 2008 set and 15 ± 1% for the 2009 set. We note that the oxygen content did not increase monotonously with storage time. This might indicate variations in sealing quality of the packaging machine(s). An alternative explanation could be that permeation through the package and/or through the exchange from product to headspace is in progress to different extents. Clear variation between the sets was measured not only in the ratio but also in the oxygen and water vapour $L_{eq}$ (see top part of Figure 4). Different sampling volume because of scattering and absorption properties or filling variation between the sets could explain this behaviour. However, the sample sets showed no large variations in weight: 275.4 ± 0.9 g for set 1, 272.2 ± 1.0 g for set 2 and 272.4 ± 0.3 g for set 3.

Figure 4. $L_{eq}$ of oxygen and water vapour as well as the ratio of oxygen and water vapour $L_{eq}$ for the three packages from the different expiration date sets. The values presented are averaged data of three measurements performed on each package with the standard deviation.
The reproducibility test with three consecutive measures on each sample showed no large variation. The ratio parameter varied on average 3% between the measurements. A deviation of the ratio of 3% corresponds to a change in oxygen concentration of 0.45 percentage units (using 15% oxygen as obtained for set 1).

**DISCUSSION**

This study examined oxygen in packaging headspace using the GASMAS method. The study augments previous results, first by showing good reproducibility and second by demonstrating the applicability to MAP employing non-transparent packages. An alternative gas to be monitored is nitrogen, but this gas does not exhibit any absorption lines that can be studied with diode laser spectroscopy.

A requirement for gas monitoring with the GASMAS technique is that laser light must be able to travel through the sample, to some extent, and interact with the gas. In this study, about 0.1% of the incident laser light (i.e. 1 μW) was transmitted through the package and detected. It should be noted that the translucency of materials is different and varies with wavelength. For example, metal films are not translucent at all, and liquid water is only translucent below 1400 nm (i.e. in the visible and near infrared regime).

The GASMAS technique is of particular interest for the food packaging industry because it could be of considerable practical importance as a non-intrusive real-time gas monitoring of non-transparent packages. The simplicity and low cost of a GASMAS instrument make it a suitable tool for quality control of food packages for both in-line and point measurements. Monitoring of packages produced in a packaging line could be done by selecting representative samples for manual inspection with an industrial version of the present set-up. Thus, unless this ambient atmosphere is displaced by nitrogen flushing, for example, or unless transparent solid light-transporting adaptors in close vicinity of the packages moving on the production line are used, large signal offsets would be recorded. Robotic positioning of the light transmission and detector units on suitable surfaces of the moving packages, with cyclic in-line synchronous following, is one alternative. The ability to carry out such
measurements non-intrusively indicates the potential of introducing food quality measurements in the packaging production line as well as in the distribution chain, because the non-intrusive way of measuring allows for repeatable measures over time on the same sample. It would for example be valuable to implement the technique in the packaging machine or on the conveyor belt after the filling line in order to make measurements continuously in the production.

CONCLUSION

Results are presented from measurements showing the feasibility of the GASMAS technique as a powerful tool for studying the gas composition as a means of quality assurance of liquid food products and carton food packaging, performed non-intrusively and over time. The experiments indicate that the GASMAS technique can be used for the important problem of securing food safety by monitoring the quality of liquid food products in modified or ‘air tight’ packages at different steps in the food supply chain and at different times after packaging. Measurements on high-quality orange juice packages with modified atmosphere illustrate the possibility to non-intrusively monitor the oxygen content and the water vapour content in liquid food packaging over time. The use of normalization through water vapour monitoring to gain absolute oxygen concentration values is also demonstrated. In addition, the measurements indicate a possibility to measure package integrity or tightness non-intrusively based on gas composition measurements.

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