Food Control 33 (2013) 162–165

Contents lists available at SciVerse ScienceDirect

Food Control

journal homepage: www.elsevier.com/locate/foodcont

The use of oxygen content determination method based on fluorescence quenching for rapeseed oil shelf-life assessment

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ARTICLE INFO

Article history:
Received 6 January 2013
Received in revised form
20 February 2013
Accepted 21 February 2013

Keywords:
Fluorescence quenching
Intelligent packaging
Modified atmosphere
Oxidation
Oxygen indicators
Shelf-life

ABSTRACT

The knowledge of the storage characteristics over the intended shelf-life period is in the interest of the manufacturing companies and it follows from the requirements of consumers, retailers and law regulations. The aim of the study was an attempt to use non-invasive oxygen determination method based on fluorescence quenching to evaluate the shelf-life of rapeseed oil.

The subjects of investigation were refined rapeseed oil samples stored at different temperature conditions (20, 40, 50 and 60 °C) under ambient air and modified atmosphere (50 °C). The samples were analyzed periodically for hydroperoxides using the iodometric method and for the oxygen content in the headspace (with the use of OxySense® 325i system).

The results show that lipid degradation during storage was accompanied by oxygen loss in the headspace. The relationship between peroxide value and oxygen concentration fitted the polynomial models. The fluorescence quenching method of oxygen determination may be a suitable and rapid tool for non-destructive shelf-life evaluation of edible oils. In packaging with pure nitrogen, oxygen indicators provide valuable information on the correctness of the packaging process.

1. Introduction

Lipid oxidation is a major cause of quality deterioration in some kinds of foods during processing and storage. Oxidative processes affect sensory, nutritional and health value of food products and as a consequence – their shelf-life (Blackburn, 2000; Dobarganes & Marquez-Ruiz, 2003; Fu & Labuza, 1993; Guillen & Goicoechea, 2008; Sucan, 2004). The knowledge of the storage characteristics over the intended shelf-life period is in the interest of the manufacturing companies and it follows from the requirements of consumers, retailers and law regulations.

Numerous analytical methods are used for assessing lipid oxidation in food and may lend themselves to monitor the shelf-life during storage. Each assay shows both the advantages and disadvantages and there is no universal method for measuring lipid oxidation. Most of used oxidation testing methods are time- and reagents-consuming and require a lot of experience from labor staff. Unfortunately, most of them are also invasive (Choe & Min, 2006; Lampi, Piironen, Hopia, & Koivistoinen, 1997; Smolander, Hurme, & Ahvenainen, 1997).

Indicated problems and limitations resulted in looking for non-destructive methods that allow to monitor the shelf-life during storage of products without removing them from the shelf. One of the solution of this problem are so-called intelligent packaging systems attached to packages as labels or incorporated directly into packaging material to monitor product quality, trace the critical control points and track product history (Han, Ho, & Rodrigues, 2005). They are used in a form of various indicators such as time/temperature integrators, oxygen and humidity or ethylene indicators, leak detectors. However these indicators are indirect because they base on polymerization rate, diffusion speed, chemical or enzymatic reaction, hence not precise. More desirable are direct indicators, especially selective sensors, which allow to control specific substances (e.g. oxygen, carbon dioxide, hydrogen sulfide, etc.) which have the significant influence on food quality and stability (Borchert, Hempel, Walsh, Kerry, & Papkovsky, 2012; Gontard, 2004; O'Mahony, O'Riordan, Papkovskaia, Kerry, & Papkovsky, 2006; Puligundla, Jung, & Ko, 2012).

In recent years there has been dedicated non-invasive oxygen determination method developed based on fluorescence quenching of specific optical sensors sensitive to oxygen (Mills, 1997, 2005; Wolfbeis & Weidgans, 2006). The method was validated and

Abbreviations: PV, peroxide value.

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http://dx.doi.org/10.1016/j.foodcont.2013.02.028

implemented to common use in 2008 as ASTM F2714-08 standard. Accordingly dedicated commercial measurement equipment was developed (e.g. Oxysense, OpTech-O_2 Platinum). In this method partial oxygen pressure inside packaging is evaluated as the derivative of fluorescence lifetime of specific oxygen indicator – ruthenium or platinum complex. Fluorescence lifetime is an average time between the absorption of an exciting light and the light emitted by excited oxygen sensor. It is inversely proportional to the oxygen partial pressure which in this study decreases along with the progress of fatty acids oxidation.

Although the fluorescence quenching method is still being developed, comprehensive evaluation for food applications has not been done so far. There is a need for research on its utility for quality assessment including evaluation of food lipids oxidation. The aim of this study was an attempt to use non-invasive oxygen determination method based on fluorescence quenching to evaluate the shelf-life of rapeseed oil. As the shelf-life limiting criterion the peroxide value was used and then referred to the oxygen loss.

2. Materials & methods

2.1. Materials

The subjects of investigation were model samples prepared with the use of commercially available refined rapeseed oil (Z.T. Kruszwica S.A., Poland), sold in PET bottles. The initial peroxide value (1.3 meq O_2/kg) was determined as described in Section 2.3, acid value (0.1 mg KOH/g) according to PN-EN ISO 660:2010. 80-mL portions of rapeseed oil were placed in 315 mL glass jars with twist-off lids. The jars were of diameter 56 mm (surface area/volume = 24.5 cm^2/80 cm^3 = 0.31). The samples were closed and stored at 20 °C and at higher temperatures – respectively: 40 °C, 50 °C and 60 °C under dark conditions. Besides samples stored under normal atmosphere (air), additional jars with oil were filled with pure nitrogen (5.0 purity) and certified gas mixture (95%N_2+5%O_2) supplied by Linde AG, Poland. The samples with modified atmosphere were stored at the temperature 50 °C in the dark. The samples stored under ambient air (50 °C) were used as the control ones. Desired atmosphere in the jars was achieved by filling them with above mentioned gases through barbed on/off valves (commonly used for sampling bags) mounted to each jar lid. All samples were prepared as a set of three for each measuring point. Periodically the samples were withdrawn to perform the measurements of oxygen content in the jars' headspace and then – the analyzes of hydroperoxides in oil. The sampling interval was dependent on storage temperature.

2.2. Oxygen content determination

The oxygen in jars' headspace was determined using OxySense® 325i system consisted of oxygen concentration analyzer and EasAlign™ pen with built-in temperature sensor. The OxySense® 325i system is a non-invasive oxygen determination instrument for the partial pressure of oxygen that is based on the effect of oxygen on fluorescence lifetime of an optically excited Tris (4,7- biphenyl 1,10- phenanthroline) ruthenium chloride complex immobilized in a highly stable polymer in a form of OxyDot® oxygen indicator. It absorbs short blue light pulses (~1 μs) emitted from the LED source and then emits red light in the absence of oxygen. If oxygen is present, its molecules collide with the excited ruthenium molecules, and the fluorescence is dynamically quenched.

The OxyDot® indicators were placed in the headspace of the sample jars using transparent adhesive. Then actual calibration of the sensors placed in the jars was performed using pure nitrogen (5.0 purity) and ambient air as standards. The particular samples were measured at room temperature with the EasAlign™ pen placed in special holder at a right angle to the surface of the jars' walls. All measurements were repeated three times and the results were calculated as an average.

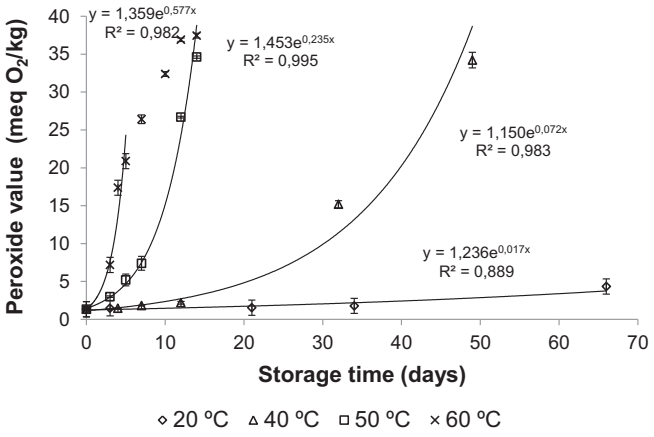

Fig. 1. Effect of storage time and temperature on the formation of hydroperoxides in rapeseed oil samples.

2.3. Hydroperoxides determination

In order to evaluate the shelf-life of oil, hydroperoxides were determined by iodometric method according to EN ISO 3960:2010 and expressed as peroxide value (PV) in meq O_2/kg of oil. All analyzes were conducted twice and the results were calculated as an average.

3. Results and discussion

The influence of time and temperature on hydroperoxides formation in rapeseed oil is presented in Fig. 1. The PVs increased during storage as the lipid degradation occurred. Processes of rapeseed oil autoxidation depended on temperature which had accelerating effect on deteriorative processes – the extent of oxidation was higher the higher was the temperature of storage. After 5 days of storage at 60 °C the rate of hydroperoxides formation decreased. It might have occurred in a result of very intense decomposition of hydroperoxides or because of oxygen consumption in the headspace (Frankel, 1998, chap. 6).

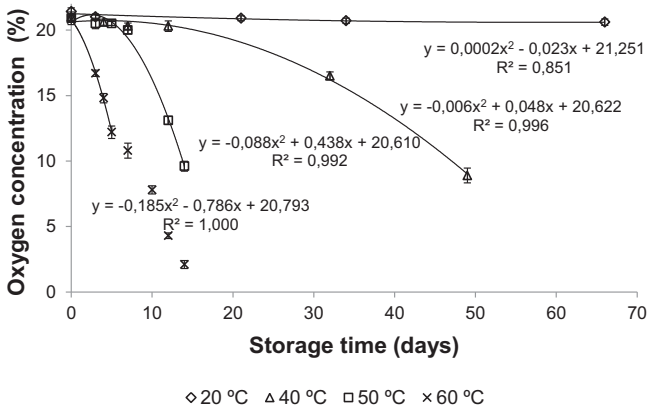

Fig. 2. Oxygen concentration changes during storage of rapeseed oil samples at temperatures 20 °C, 40 °C, 50 °C and 60 °C.