Effect of Fluorescent Light and Light Emitting Diode Illumination on Volatile Profiles of Vegetable Oils

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Abstract Volatile compounds from vegetable oils under lighting emitting diode (LED) illumination were analyzed during 12 weeks of storage using different containers. Pattern changes in volatile compounds were analyzed using an electronic nose based on MS. Vegetable oils were more influenced by container type than by illumination. The greatest change in volatile compounds was observed with use of polyethylene (PE) bottles. Amber bottles provided a light blocking effect during early stages of storage that decreased in strength after 12 weeks. Volatile components of vegetable oils were most influenced under fluorescent and blue LED illumination. In contrast, least changes in volatile contents was observed under red and green LED illumination. Appropriate LED colors and container types can provide good quality vegetable oil under a distribution chain system.

Keywords: lighting emitting diode, fluorescent light, electronic nose, vegetable oil

Introduction

Vegetable oils are affected by light, temperature, oxygen, metal, and other factors, leading to oxidation, hydrolysis, polymerization, and other chemical reactions that affect the oil quality (1). Oxidation results in off-flavors, color fading, loss of flavor, and loss of important nutrients (2). If these changes occur during distribution or consumption, oil quality and consumer health will be compromised.

Soybean oil is generally sold in polyethylene (PE) or polyethylene phthalate (PET) bottles. Sesame oil and perilla oil are generally sold in either transparent or amber glass bottles. Based on studies of packaging effects on vegetable oil quality, a strong correlation exists between packaging material and oil stability and between transmission rates of O₂ and H₂O and percent transmission of light (3-5) that have influenced the vegetable oil quality of shea butter (6) and crude palm oil (7). Therefore, in order to minimize changes in vegetable oil quality, light transmittance must be taken into consideration for selection of an appropriate packaging material.

Many studies have investigated the relationship between lighting emitting diode (LED) illumination and food preservation. The organic acid content of kiwi fruit decreased under white, red, and green LED illumination, shortening the after-ripening period (8). An increase in light intensity for edible oils caused discoloration of fat and accelerated oxidation (9). However, there is a limit to which light intensity can be lowered under a display for sale distribution chain system. Six different vegetable oils were studied for 35 weeks under red, yellow, and blue LED light and fluorescent light, and the greatest

degree of change in volatile components was observed under fluorescent light (10), leading to the conclusion that use of a single color LED rather than fluorescent light results in fewer changes in the quality of fat. Meanwhile, soybean oil in PE bottles showed a great change in volatile components under fluorescent light and blue LED illumination, and showed the second least degree of change under green LED illumination, second only to darkness (11).

One of the changes in vegetable oil quality is generation of an off-flavor. Changes in oil quality can be examined based on an off-flavor that represents changes in volatile components. One method for monitoring of volatile components is use of an electronic nose that allows elimination of all pretreatment processes, thereby allowing continuous, non-destructive analysis (12). Also, the electronic nose detects minute amounts of components that cannot be detected using GC and GC/MS (13). Studies of changes in the quality of vegetable oils using an electronic nose have been performed for measurement of the degree of fat oxidation in palm oil (14) and rape seed oil (15). Shen *et al.* (16) analyzed canola oil, corn oil, and soybean oil and showed that amounts of volatile components increased as the storage time increased.

Previous studies have used only a single container type or a single light condition. There has been little study of the effects of complex conditions using different LED colors and containers. Because different vegetable oils have different qualities, oils need to be studied using different containers. The objectives of this study were to determine proper containers for vegetable oils, and to determine LED irradiation with the least influence under sale display conditions.

Materials and Methods

Oil types Soybean oil (Sajohaepyo, Seoul, Korea) with a shelf-life of 2 years, sesame oil (Beksul; CJ Cheiljedang, Seoul, Korea) with a shelf-life of 2 years and perilla oil (Sajohaepyo) with a shelf-life of 1 year were used in this study. Oils obtained in light protective boxes were stored under darkness.

Container types Each oils was stored in different containers. 10 mL transparent glass bottle (La-Pha-Pack® GmbH, Langerwehe, Germany) and sealed using a PTFE/rubber cap (Pharma-Fix, Chemmea, Slovakia), 10 mL amber glass bottle (9-425 screw top, LBSV002A; Membrane Solution, LLC., North Bend, OH, USA) and sealed using a PTFE/silicone using a septa screw cap (LBSV002CRS; Membrane Solution, LLC.), PE bottle (LDPE; SHINDO Industry Co., Ltd., Gimpo, Korea) and sealed using a PE cap (LDPE; SHINDO Industry Co., Ltd.).

Storage conditions and LED equipment Soybean oil, sesame oil, and perilla oil were placed in an incubator (VS-1203P3N; Vision Scientific Co., Ltd., Daejeon, Korea) at 25°C under each light condition. Measurement of volatile components was carried out after 4, 8, and 12 weeks. The darkness condition was achieved by covering the rack where all oil samples were maintained with aluminum foil.

Dimensions of LED equipment used were reported by Park *et al.* (11). Wavelengths for each light source showed the greatest degree of absorption at 370–630 nm for fluorescent light, at 410–480 nm for white LED, at 420–290 nm for blue LED, at 490–560 nm for green LED and at 600–650 nm for red LED.

Electronic nose analysis Oil samples were prepared for analysis by placing 1 g of each oil sample into a 10 mL vial (La-Pha-Pack® GmbH) and sealing with a PTFE/silicone cap (Pharma-Fix). An electronic nose was connected to an autosampler (CombiPAL; CTC Analytics, Zwingen, Switzerland) and an MS apparatus (Quadrupole Mass Spectrometer, Balzers Instruments, Marin-Epagnier, Switzerland). Analysis followed the method of Park *et al.* (11).

Discriminant function analysis (DFA) Of the 10–200 amu ionic fragments produced from volatile components, $m/z=15$ –30 fragments with a high degree of differentiation were used as independent variables for a discriminant function analysis (DFA) performed following the method of Park *et al.* (11) with results based on calculation of the sensitivity of the selected variables. The 10 to 20 variable groups with highest Mw values were subjected to statistical analysis using SMarT Nose® statistical analysis software (Version 1.51, Thopas Soft Creation, Marin-Epagnier, Switzerland).

Results and Discussion

Analyzed volatile patterns of vegetable oils at 4, 8, and 12 weeks

Fig. 1. DFA plot based on electronic nose results for soybean oil in PE bottles under fluorescent light illumination and darkness conditions for 12 weeks.

were compared with a control group of oil samples at week 0. DFA results were illustrated in a 2-dimensional graph with the x-axis being the first discriminant function score (DF1) and the y-axis the second discriminant function score (DF2). Intervals between oil samples on DFA graphs represented differences between oil samples. Based on studies using an electronic nose, volatile components change with an increasing distance from the control group (11,15,17).

Effects of light Effects of light on soybean oil are shown in Fig. 1 with oil samples at week 0 as controls. Soybean oil samples were stored under fluorescent light illumination and darkness in PE bottles for 12 weeks. The F value represented the discriminant power for differences between oil samples. As the F value increases, the influence of decision also increases. F values for DF1 and DF2 were 864.24 and 66.61, respectively. DF1 exerted an influence 13x stronger than DF2. Therefore, differences between oil samples seen in Fig. 1 were generally determined based on DF1.

Under both fluorescent light illumination and darkness the volatile component content increased with a longer storage time. For oil samples stored in darkness, no significant ($p<0.05$) change was observed for the DF1 value between fluorescent light illumination and darkness. However, a significant ($p<0.05$) change of volatile patterns was observed for the DF2 value between fluorescent light illumination and darkness so the degree of change was relatively small. On the other hand, oil samples under fluorescent light illumination displayed a significant ($p<0.05$) change, compared with darkness conditions. Also, there was a gradual change in the DF1 value in relation to the storage time.

Therefore, a positive correlation existed between the storage time and the level of change in volatile components. Under darkness, there was little change in volatile components, but a big change was observed under fluorescent light. Kim *et al.* (10) also reached a similar conclusion, noting that when measured using the electronic nose, 6 types of vegetable oil showed a much greater degree of change in volatile components under fluorescent light than under darkness. In addition, seaweed (18) and frozen beef (19) yielded

undesirable results under fluorescent light, compared with darkness.

Changes in volatile patterns due to illumination wavelengths Oil samples stored in transparent glass bottles were analyzed for determination of the influence of light wavelengths. Changes in volatile components due to wavelengths are shown in Fig. 2. F values of DF1 and DF2 were 173.50 and 11.94, respectively, (Fig. 2A). The influence of DF1 was approximately 14.5x stronger than DF2. F values of DF1 and DF2 were 5,543.50 and 177.26, respectively, (Fig. 2B) with DF1 being 31x larger than DF2. Lastly, F values of DF1 and DF2 were 466.38 and 270.62, respectively, (Fig. 2C) with a difference of 1.7x. Thus, the level of dependency for DF1 on differentiation was higher than for DF2, indicating the key role of DF1 in oil volatile content differences.

Soybean oil (Fig. 2A) showed a big change in volatile components only under fluorescent light illumination. Under LED and darkness conditions, soybean oil showed only small changes that were difficult to differentiate. Sesame oil (Fig. 2B) under blue LED illumination exhibited a bigger change. There was barely any change in the volatile components in oils under red LED and under darkness. Oils under red LED and darkness were closely located to control oils. For perilla oil (Fig. 2C), a similar pattern was observed with the biggest changes of volatile patterns observed under fluorescent light and blue LED illumination in comparison with control oils. Oils under green LED illumination and darkness did not show any significant difference between DF1 values.

Although soybean oil was only substantially affected by fluorescent light, sesame oil and perilla oil displayed big changes under fluorescent light and blue LED irradiation. Moreover, responses of sesame oil and perilla oil also generally similar under different LED illumination. All vegetable oils exhibited the least influence under darkness conditions. Sesame oil and perilla oil were little affected by red and green LED illumination, respectively.

The greatest change in the volatile components of whole milk reportedly occurred under blue LED illumination (17). Sesame oil was affected more under blue LED illumination than under yellow or red LED, or fluorescent light as the storage time increased (20).

Effects of containers Volatile patterns of sesame oil analyzed after storage in three different bottle types for 4 weeks are shown in Fig. 3. F values of DF1 and DF2 were 3,490.60 and 436.45, respectively (Fig. 3A). The influence of DF1 was 8x greater than DF2.

Compared to oils in glass bottles, oils stored in PE bottles located compositionally far from control oils were observed to be in the negative slope direction (Fig. 3A). Thus, sesame oil stored and distributed in PE bottles suffered changes in volatile components at all wavelengths. Darkness conditions elicited no changes. On the other hand, oils stored in glass bottles showed little difference from control oils. Thus, fewer changes in volatile components occurred with storage in glass bottles than in PE bottles due to differences in container properties.

Fig. 2. DFA plot based on electronic nose results for vegetable oils in transparent glass bottles under different LED and fluorescent light illumination conditions and darkness for 12 weeks. (A) soybean oil, (B) sesame oil, (C) perilla oil.

Under sunlight, crude palm oil exhibited differences based on the type of container used for storage (7) due to the higher total oxidation values of clear plastic bottles in comparison with amber, green, and clear glass bottles, similar to results of this study where more change in vegetable oil quality in plastic bottles was observed than in glass bottles. However, the possibility of an influence from interactions between plastic containers and vegetable oils should also be taken into account in the future.

DFA values of oil samples stored in glass bottles are plotted in Fig. 3. F values of DF1 and DF2 were 780.95 and 35.61, respectively, with the F value of DF1 being 22x greater (Fig. 3B). Compared with oil samples in amber glass bottles, oil samples in transparent glass bottles were compositionally farther away from control oils in the negative direction, indicating that oils in transparent glass bottles

Fig. 3. DFA plot based on electronic nose results for sesame oil in different bottle types under different LED and fluorescent light illumination conditions and darkness for 4 weeks. (A) PE, transparent glass, amber glass bottle, (B) transparent glass, amber glass bottle. PE=polyethylene bottle, T=transparent glass bottle, A=amber glass bottle.

exhibited more changes in volatile components than in oils in amber glass bottles. Oils stored in amber glass bottles were relatively compositionally close to control oils and showed little change in volatile components. Thus, the container type exerted a bigger influence than the light wavelength.

A previous study of shea butter reported that oil samples stored in clear colorless bottles exhibited a higher free fatty acid content and peroxide value than oil samples stored in amber bottles (6). Also, oil samples in clear colorless bottles experienced more rapid oxidation than in amber bottles, and total oxidation values of crude palm oil in clear glass bottles were much higher than for amber glass bottles (7), both similar to results reported herein. Thus, similar results can be attributed to the light-blocking effect of amber glass bottles. PE bottles should not be used for storage of vegetable oil and amber glass bottles provide better oil stability than transparent glass bottles.

Stability of vegetable oils in containers Oils stored in a different containers underwent changes as the storage time increased with results shown in a 2-dimensional graph with the DF1 value as the x-axis and storage time as the y-axis (Fig. 4). Differences between oil samples stored under fluorescent light and blue LED, and under green LED and darkness was compared. Fluorescent light and blue

LED illumination elicited the most changes in the volatile components of vegetable oils.

Oil samples stored in PE bottles were affected after 4 weeks under all light conditions compared with time 0. Therefore, PE bottles are not recommended as containers for vegetable oils.

During the first 4 weeks of storage, oils in transparent glass bottles showed changes in volatile components under fluorescent light. In the period between 4 to 8 weeks, soybean oil (Fig. 4A) exhibited more change than other oil samples under fluorescent light. Big changes in volatile components were observed in sesame oil (Fig. 4B) and perilla oil (Fig. 4C) under fluorescent light and blue LED. After 8 weeks, only darkness conditions failed to affect the volatile components of oils.

During the first 4 weeks, oils stored in amber glass bottles showed less change in volatile components than for other bottle types under all light conditions due to the light-blocking effect of amber glass. Between weeks 4 to 8, soybean and sesame oils showed a similar amber glass blocking effect, but perilla oil (Fig. 4F) showed no such effect under blue LED illumination.

After the first 8 weeks, all vegetable oils underwent changes in volatile components with soybean oil exhibiting the most change under fluorescent light illumination. Sesame oil (Fig. 4E) showed large changes under blue LED illumination and, at 12 weeks, the level of change exhibited under blue LED illumination was close to the level of change under fluorescent light. Thus, blue LED illumination, which was blocked for the first 8 weeks, was no longer effectively blocked and volatile components were affected. Perilla oil (Fig. 4F) was affected by blue LED illumination and perilla oil under fluorescent light illumination also started to exhibit changes after 8 weeks.

Oils in transparent glass bottles were subject only to particular wavelengths such as fluorescent light during the first 4 weeks of storage, after which more wavelengths started to have an effect. After 8 weeks of storage, all light conditions except darkness exerted an influence. Amber glass bottles displayed an excellent light-blocking effect for all 3 vegetable oils from the beginning of storage. However, after the first 4 weeks, the effect faltered for particular wavelengths such as blue LED and fluorescent light and, starting at 8 weeks, almost all light conditions except darkness exerted some type of influence.

According to Leo (3), compared to glass, high density polyethylene (HDPE) provides a weaker oil stability property for storage with much higher degrees of O_2 and H_2O permeability than glass, prompting the conclusion that the stability of oil in HDPE packaging lasts only for 3 to 6 months. Among different types of glass, amber reportedly provided a greater stability for oil than flint glass (transparent glass), and flint glass showed a greater transmission percentage for visible light (3,5). The transmission percentage for amber glass is 5.9% at 350 nm, 2.7% at 400 nm, and 29.9% at 580 nm, indicative of an excellent visible light blocking property for short wavelengths (4), in agreement with results of this study.

Fig. 4. DFA plot based on electronic nose results for vegetable oils under LED illumination and darkness for 12 weeks. (A) soybean oil, (B) sesame oil, (C) perilla oil in transparent bottles, (D) soybean oil, (E) sesame oil, (F) perilla oil in amber bottles.

Amber glass bottle provided the best stability against changes in lipid quality in this study from the beginning of the storage period. However, the light blocking effect started to decline in effectiveness after 8 weeks. Therefore, in order to effectively store vegetable oils for a long time, an appropriate light source needs to be used.

Effect of containers and wavelengths Wavelength influences changed in response to different containers (Fig. 5 and 6). Results for vegetable oils stored in amber glass bottles are shown in Fig. 5. Soybean oil stored in amber bottles (Fig. 5A) showed large changes under fluorescent light. Sesame oil stored in amber glass bottles showed the most change in volatile components under fluorescent light and blue LED illumination. On the other hand, relatively little change was observed under green and red LED illumination. Perilla oil stored in amber glass bottles (Fig. 5C) showed the greatest change under blue LED and fluorescent light illumination and little change under other LED conditions and under darkness. Volatile changes in amber bottles were similar to changes in transparent bottles (Fig. 2).

Results for oils stored in PE bottles are shown in Fig. 6. Soybean oil stored in PE bottles (Fig. 6A) underwent the most change under fluorescent light, followed by blue LED conditions. However, soybean oil showed little change under red or green LED and darkness conditions, similar to a report of Park *et al.* (11) where soybean oil placed in PE bottles showed large changes in volatile components under fluorescent light, and blue and white LED illumination.

Sesame oil in PE bottles (Fig. 6B) showed changes under fluorescent light and blue LED illumination after 12 weeks. Soybean and sesame oils stored in PE bottles were equally affected by different wavelengths, unlike oils stored in transparent and amber glass bottles.

Perilla oil stored in PE bottles (Fig. 6C) showed the most change under blue LED illumination. However, under fluorescent light, perilla oil in PE bottles showed fewer changes in volatile components compared with transparent bottles (Fig. 2C) and amber glass bottles (Fig. 5C), probably due to the nature of PE bottles with high O₂ and H₂O transmittance rates, and an ability to interact with vegetable oils. Thus, oils stored in PE bottles showed large changes in volatile components from week 4 of storage.

Compared with soybean and sesame oils, perilla oil was strongly influenced by different LED colors and, therefore, exhibited changes in volatile components. Perilla oil has a high linolenic acid content that is 50-60% higher than for any other edible oil. Linolenic acid is chemically unstable and, thus, easily suffers oxidation in the presence of oxygen (21). On the other hand, soybean oil contains tocopherol, and sesame oil contains sesamol, sesamin, and sesamol. These antioxidants increase the auto-oxidative stability of unsaturated fatty acids, such as linoleic acid (22), and may be the reason perilla oil stored in PE bottles for 12 weeks (Fig. 6C) underwent more change than other vegetable oils. It is possible that most changes in volatile components under fluorescent light occurred during the early stages of storage with no subsequent change, while change was detected under other LED conditions.

Fluorescent light and blue LED illumination should not be used for vegetable oil storage. The most suitable storage condition was darkness. Appropriate light conditions for vegetable oils were red and green LED.

Blue LED illumination has short wavelengths while green and red LED illumination has longer wavelengths. In this study, short wavelength light sources caused more changes in volatile components than long wavelengths. Short wavelength LED illumination was more

Fig. 5. DFA plot based on electronic nose results for vegetable oils stored in amber glass bottles under different LED and fluorescent light illumination and darkness for 12 weeks. (A) soybean oil, (B) sesame oil, (C) perilla oil.

influenced by light energy and transmission than long wavelength LED. Changes in the quality of food due to short wavelengths has been reported. Blocking 446 nm delays production of volatile components in milk (23), in agreement with Sherwin (24) that vegetable oils are unstable under short-wavelength illumination. Fluorescent light includes a complete range of all visible short and long wavelengths causing changes in volatile components similar to changes caused by short wavelength LED.

Soybean oil should not be stored in plastic bottles for long term storage. Sesame and perilla oils have high polyhydric unsaturated fatty acid contents, and perilla oil has a lower antioxidant content than sesame oil. Therefore, both are more vulnerable to quality change with long term exposure to light. Use of either amber glass

Fig. 6. DFA plot based on electronic nose results for vegetable oils stored in PE bottles under different LED and fluorescent light illumination and darkness for 12 weeks. (A) soybean oil, (B) sesame oil, (C) perilla oil.

bottles or cans for storage of sesame and perilla oils is indicated.

From the wavelength aspect, soybean oil is vulnerable to fluorescent light wavelengths, and sesame and perilla oils are vulnerable to both fluorescent light and short wavelength LED. The most suitable storage condition for soybean and perilla oils is darkness. The most suitable light conditions for vegetable oils are red and green LED. A high level of eco-friendly, fresh, and good quality vegetable oils can be achieved with application of the light conditions suggested herein.

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