Determination of oxidized edible oils by near infrared spectroscopy

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Introduction

Near infrared (NIR) techniques have been widely used for quantitative analyses of many food components, such as moisture, protein, carbohydrate, and lipid. NIR is also used to determine the quality of foods. In our laboratory, spectral analysis for protein determination by NIR has been studied for years.[1–4] Lipid is also an important nutrient and is easily deteriorated by oxidation and hydrolysis. Determinations of lipid oxidation and stability using mid-infrared has been reported,[5–7] however, these methods are not yet commonly adopted. In addition, a NIR method for determination of fatty acid composition has been reported.[8] However, a NIR technique has not been reported for determining the deterioration of lipids. In this study, we have found a specific absorption peak of lipid peroxides and developed a method for determination of oxidized edible oils by NIR spectroscopy using peroxide value (*POV*) as the index of oxidation.

Materials and methods

Materials

Soybean, cotton seed, olive, corn, canola and high-erucic rapeseed oils were used after removing tocopherols by column chromatography. Methyl oleate and methyl linoleate were also used. These oils and fatty acid methyl esters were oxidized by auto-oxidation or UV-induced oxidation.

NIR determination

NIR transmittance spectra of lipids were determined in 1 mm cuvette cell using the NIRSystems (Pacific Science) Model 6250 research composition analyzer at 30°C. Regression analysis was carried out by using NSAS software (Ver. 3.18) of NIRSystems.

POV determination

POV was determined according to the method of Asakawa and Matsushita.[9]

Results and discussion

Change in NIR spectra of oxidized oils

Figure 1 shows the raw spectra (a), the second derivative spectra (b) and the differential second derivative spectra (c) of oxidized soybean oil. The raw spectra are too broad to show the spectral changes by oxidation. The second derivative spectra show the absorption peaks due to oxidization. However, these peaks were small compared to other peaks. The differential second derivative spectra, which were calculated by subtracting the second derivative spectrum of unoxidized oil,

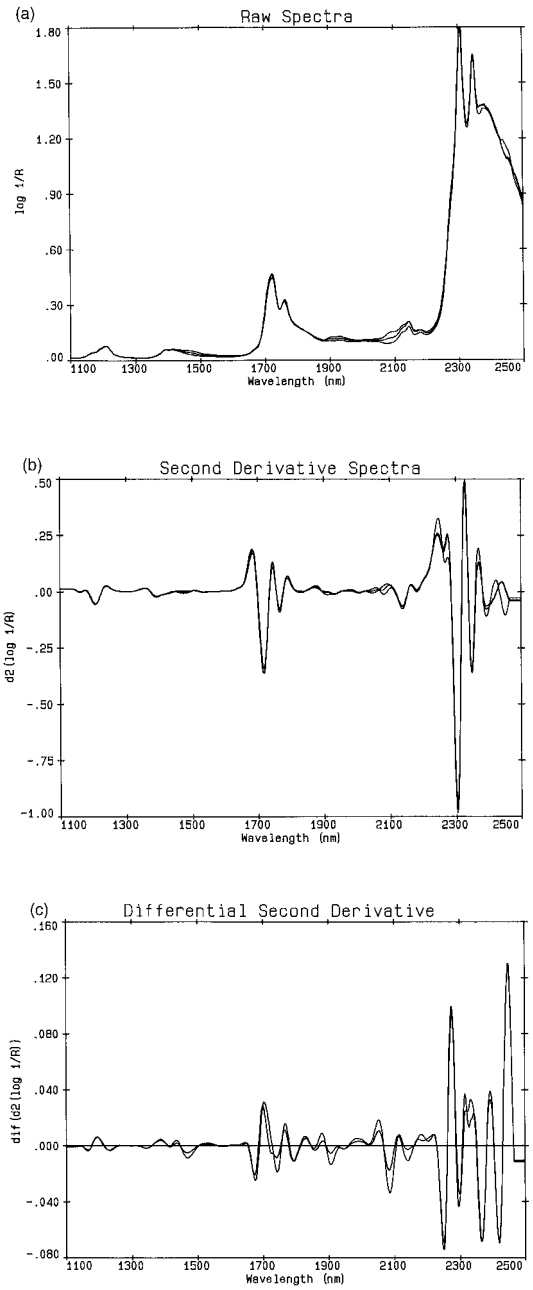

Figure 1. NIR spectra of unoxidized and oxidized soybean oils. The raw spectra (a), the second derivative spectra (b) and the differential second derivative spectra (c) of unoxidized and oxidized (*POV* = 1250 and 2500) soybean oils are shown. The differential second derivative spectra were calculated by subtracting the second derivative spectrum of unoxidized oil.

Table 1. Correlation between NIR second derivative spectra and POV of oxidized oils.

Soybean			Cotton seed			Olive		
nm	K_1	R	nm	K_1	R	nm	K_1	R
1468–1470	–64197	–0.996	1470	–68131	–0.999	1468	–77719	–0.990
2084	–12904	–0.987	2084	–13772	–0.996	2084	–15686	–0.992
Corn			Canola			High-erucic rapeseed		
nm	K_1	R	nm	K_1	R	nm	K_1	R
1468–1470	–83356	–0.985	1470	–83295	–0.988	1468	–81652	–0.985
2086	–616834	–0.991	2086	–15830	–0.993	2086	–15277	–0.988

show the absorption peaks due to oxidation clearly. Two peaks in the negative direction, which are true peaks in second derivative spectra, were confirmed at 1468 and 2184 nm. The differential spectra of other oxidized oils were similar to that of soybean oil.

Correlation between NIR spectra and *POV* in oxidized oils

Correlation between the absorption peaks of NIR second derivative spectra and *POV* in oxidized oils was analyzed. Table 1 shows the regression coefficient (K_1) and correlation coefficient (R) values for absorption peaks of oxidized oils. Correlation coefficient values of two absorption peaks were large enough for all six oxidized oils, which suggests the possibility of using these wavelengths for *POV* determination.

Table 2. Correlation between NIR second derivative spectra and POV of oxidized and hydroperoxide-mixed oils.

Soybean					
Oxidized			Hyperoxide-mixed		
nm	K_1	R	nm	K_1	R
1468	–64197	–0.996			
2084	–12879	–0.987	2084	–11945	–0.999
Cotton seed					
Oxidized			Hydroperoxide-mixed		
nm	K_1	R	nm	K_1	R
1470	–68131	–0.999			
2084	–13772	–0.996	2084	–15267	–0.998

Correlation between NIR spectra and *POV* in hydroperoxide-mixed oils

Oxidized oils contain some kinds of secondary products as well as lipid peroxides. To eliminate the effects of secondary products, hydroperoxides were purified from oxidized oils by column chromatography and were added to unoxidized oils. Then, NIR spectra and *POV* were determined and correlation between the absorption peaks of the second derivative spectra and *POV* was analyzed. Table 2 shows the regression coefficient (K_1) and correlation coefficient (R) values for absorption peaks of oxidized and hydroperoxide-mixed soybean and cotton seed oils. This table demonstrates that 2084 nm is the only wavelength due to oil hydroperoxide and suitable for *POV* analysis.

NIR spectra of hydroperoxide and hydroxide of fatty acid methyl esters

Methyl oleate and methyl linoleate were oxidized and their hydroperoxides were purified by column chromatography. Hydroxide of methyl linoleate was synthesized by the reduction of methyl linoleate hydroperoxide with sodium borohydride. The hydroperoxides and hydroxide were added to unoxidized methyl linoleate. Then, NIR spectra and *POV* were determined. The

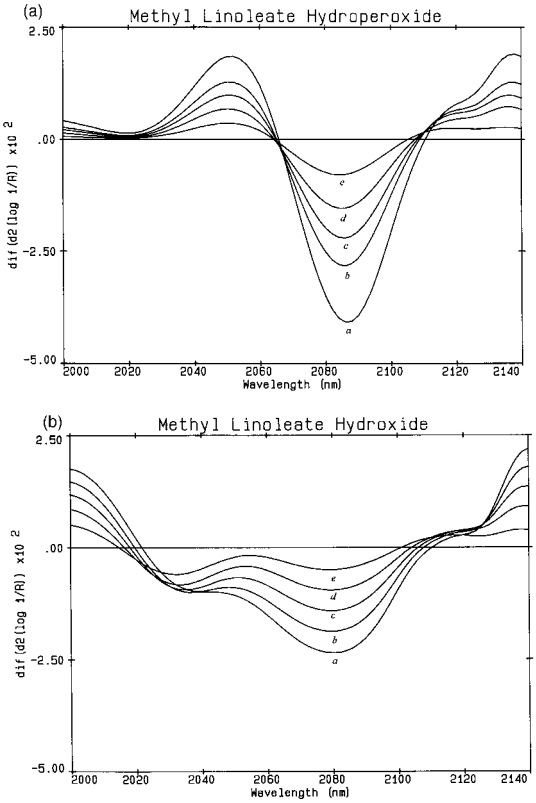

Figure 2. The differential second derivative spectra of methyl linoleate hydroperoxide and hydroxide mixed with methyl linoleate. The differential second derivative spectra of methyl linoleate hydroperoxide (a) and hydroxide (b) mixed with methyl linoleate are shown. Lines a–e in (a) correspond to lines a–e in (b). *POV* range of hydroperoxide mixture was 0–3200.

absorption peak at 2084–2086 nm was highly correlated with *POV* for hydroperoxide of both methyl oleate and methyl linoleate (data not shown). The differential second derivative spectra of methyl linoleate hydroperoxide and hydroxide respectively mixed with methyl linoleate are shown in Figures 2(a) and 2(b). The peak at 2086 nm in hydroperoxide [Figure 2(a)] shifted and was weaker after reduction [Figure 2(b)]. These results demonstrates that the NIR absorption peak at 2084–2086 nm is due to the OOH group of lipid hydroperoxides, not the conjugate diene. This wavelength is specific for lipid hydroperoxide and would be useful for determination of oxidized edible oils.

Summary

The relationship between NIR second derivative spectra and oxidation of edible oils was investigated to develop a method for determination of oxidized edible oils by NIR spectroscopy, using *POV* as the index of oxidation. In the differential second derivative spectra of six kinds of oxidized edible oils, the absorption peaks at 1468 and 2084 nm were highly correlated to *POV*. In the spectra of purified hydroperoxides of oils and fatty acid methyl esters, however, 2084–2086 nm was the only wavelength with high correlation with *POV*, which demonstrates that the absorption is due to hydroperoxide. In addition, this peak shifted and was weaker after reduction of hydroperoxide to hydroxide, which shows the absorption specific for the OOH group. These results suggest that the absorption peak at 2084–2086 nm is specific for hydroperoxide and suitable for determination of oxidized edible oils.

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