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An Application of Surface Plasmon Resonance to Evaluation of Quality Parameters of Soybean Oil during Frying

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Abstract Feasibility of surface plasmon resonance (SPR) method to evaluate soybean frying oil quality was evaluated. Free fatty acid value, *p*-anisidine value, conjugated dienoic acid content, conjugated trienoic acid content, peroxide value, iodine value, total polar compound (TPC), ratio of unsaturated fatty acid to saturated fatty acid, refractive index, dielectric constant, smoking point, and L, a, and b of Hunter color system were selected as parameters related to conventional evaluation of soybean frying oil quality. SPR scale mapped with conventional quality parameters well described free fatty acid value, conjugated dienoic acid content, dielectric constant, TPC, and b of Hunter color system, as shown by correlation and linear regression analyses.

Keywords: surface plasmon resonance, soybean oil, quality parameter, frying

Introduction

Deep-fat frying is used for a large variety of foods in households, restaurants, and food manufacturing facilities, during which oil is repeatedly or continuously used at elevated temperatures, and various chemical processes such as hydrolysis, polymerization, and oxidation take place (1-3). These phenomena result in the accumulation of decomposition products that not only affect the quality of fried foods but also are of much concern to human health and nutrition (4). Accordingly, the importance of establishing simple and objective methods for quality evaluation of used frying oil cannot be overemphasized.

In spite of many assessments to measure the lipid oxidation in oils, no single method has yet been established to evaluate all oxidative qualities of frying oils due to the complexity of the reactions between lipids and other substances (5). The degree of frying oil deterioration can be measured by chemical and/or physical methods (6-8). Chemical methods include free fatty acid value, peroxide value, iodine value, *p*-anisidine value, total polar compound (TPC), and fatty acid composition. In the case of physical methods, smoking point, conjugated dienoic and trienoic acid contents, dielectric constant, refractive index, and color of oil have been used. Among these methods, determination of TPC by column chromatography (CC) has been recognized as the most reliable method (1, 9, 10). However, because conventional methods such as CC are extremely time-consuming and laborious, many attempts have been undertaken to find more rapid analytical techniques using, among others, Foodoil Sensor (FOS) (6), HPLC (8), NMR (11), electronic nose (12), FTIR (13), optical methods (14, 15), and colorimetric quick test (10). Nonetheless, measurement by quick tests of only one parameter that does not show a good correlation with the degree of degradation can be misleading.

Surface plasmon resonance (SPR), first described in the beginning of the 20th century by Wood, is a quantum-electrical phenomenon arising from the interaction of light with a thin metal surface. The potential of SPR phenomenon for the characterization of chemical and biological molecules was recognized in the late 1970s. Currently, SPR is considered as the most advanced thin film refractometric sensor technology in sensor instrumentation and applications. SPR sensor technology has a variety of SPR sensor platforms, from miniature SPR probes to robust bench-top laboratory units (16, 17).

The objectives of this study were to analyze the physicochemical properties related to frying oil quality and to find a simple and rapid method for the evaluation of soybean frying oil quality using a miniature SPR sensing unit.

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Materials and Methods

Materials Soybean oil and frozen potato sticks (1×1×5 cm) were purchased at a local market in Korea. All reagents used were of analytical grade unless otherwise specified.

Frying process Frozen potato sticks were fried for 4 min at 190±1°C in a temperature-controlled batch fryer (Princess Royal Deep Fryer, Seoul, Korea). Initially, the fryer was filled with soybean oil to the maximum level of 3 L. Every morning as soon as the temperature of oil reached 190°C, about 300 g frozen potato sticks were fried twice consecutively at a 20-min interval, because time required to reach and maintain the oil at 190°C before second frying was 20 min. The oil was then heated for 8 hr without further frying, and the fryer was turned off. Estimated total time the oil was heated without replenishment of fresh oil throughout the experimental period was 72 hr. Frying oils collected every 8 hr were stored at -20°C under N_2 gas.

Analytical methods Determination of free fatty acid (Cd 3a-63) contents, peroxide value (Cd 8-53), iodine value (Cd 1-25), *p*-anisidine (Cd 18-90), ratio of unsaturated fatty acid to saturated fatty acid by fatty acid composition (Ce-a-62), and smoking point (Cc 99-48) were carried out using the American Oil Chemists' Society (AOCS) standard procedures (18). TPC was determined by CC (15). The conjugated dienoic acid and trienoic acid contents were determined using a spectrophotometer at 232 and 268 nm, respectively (19). Dielectric constants of frying oils were measured using Foodoil Sensor NI-22 (Northern Instruments Corp., Lino-Lakes, MN, USA). Automatic Refractometer GPR 06-89 (Index instrument Ltd., Huntingdon, England) was used to measure the refractive indices of frying oils at 25°C. L, a, and b values were determined using Colorimeter Σ90 (Nippon Denshoku, Tokyo, Japan) to evaluate the color of frying oils,.

SPR instrumentation An SPR apparatus was fabricated using a Spreeta® SPR sensor (Texas Instrument, Carrollton, TX, USA), an analog-to-digital converter, a serial communicator of RS-232C, and a lap-top computer (Fig. 1). Spreeta®, a compact type SPR sensor integrated into a small container, was composed of 840 nm NIR light emitting diode with a polarizer, thin gold film, reflecting mirror, and a photodiode array with 128 pixels. The ethanol-soluble fraction of the frying oil was prepared by the method of Cho *et al.* (20) and used as the test sample. The SPR curve obtained was converted into a refractive index by calculating the 1st moment of points below the baseline of 0.80 in the SPR curve (20). The values measured by the SPR apparatus were compared to those obtained by the analytical methods.

Statistical analysis Correlation coefficient and regression were analyzed with the SAS system (SAS Institute, Cary, NC, USA).

Results and Discussion

SPR curve of frying oil and refractive index An SPR apparatus was fabricated to develop a rapid and simple method for evaluating the quality of soybean frying oil. Typical SPR curves were obtained through SPR technique only when ethanol-soluble fraction of soybean oil was used. To apply SPR technique to quality evaluation of frying oil, a sample preparation method similar to the one used in this study should be included. Figure 2a shows SPR curves obtained using the SPR apparatus. These curves shifted left with increasing frying time. When each curve was converted into a refractive index based on pure water, the value of refractive index increased with frying time (Fig. 2b).

Relation of SPR value to physicochemical properties The signals obtained by the SPR system were converted into SPR refractive indices, and mapped with 14 conventional quality parameters including free fatty acid value, *p*-anisidine value, conjugated dienoic acid content, conjugated trienoic acid content, peroxide value, iodine value, TPC, ratio of unsaturated fatty acid to saturated fatty acid, refractive index, dielectric constant, smoking point, and L, a, and b values of Hunter color. The relationships of refractive index obtained by SPR to the physicochemical properties of soybean oil and their correlation coefficients are shown in Fig. 3 and Table 1, respectively.

Among the 14 physicochemical properties, free fatty acid value, conjugated dienoic acid content, TPC, dielectric constant, and b of Hunter color showed correlation with SPR refractive index at 0.001 significant levels. Because analysis of chemical parameters such as free fatty acid value, conjugated dienoic acid content, and TPC is considered to be time-consuming and laborious, SPR method is considered as an alternative in evaluating the

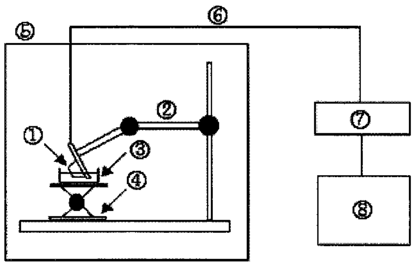

Fig. 1. Schematic diagram of a SPR apparatus. 1. SPR sensor, 2. Height-and-angle-adjustable arm, 3. Sample liquid, 4. Height-adjustable platform, 5. Dark chamber, 6. RS-232C, 7. A/D converter, 8. Laptop.

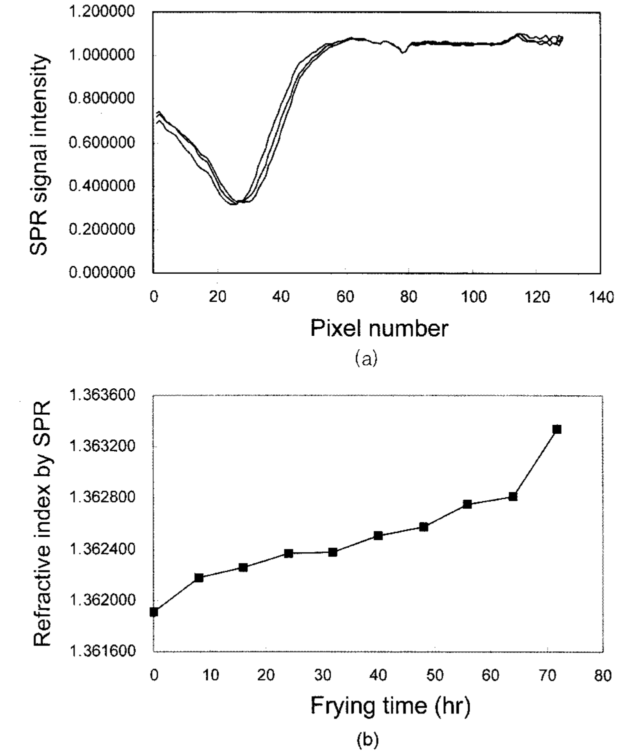

Fig. 2. (a) SPR curves for ethanol-soluble fractions of soybean oil when frying times are 0, 40, and 72 hr, (b) refractive indices induced from SPR curves during 0 to 72 hr frying.

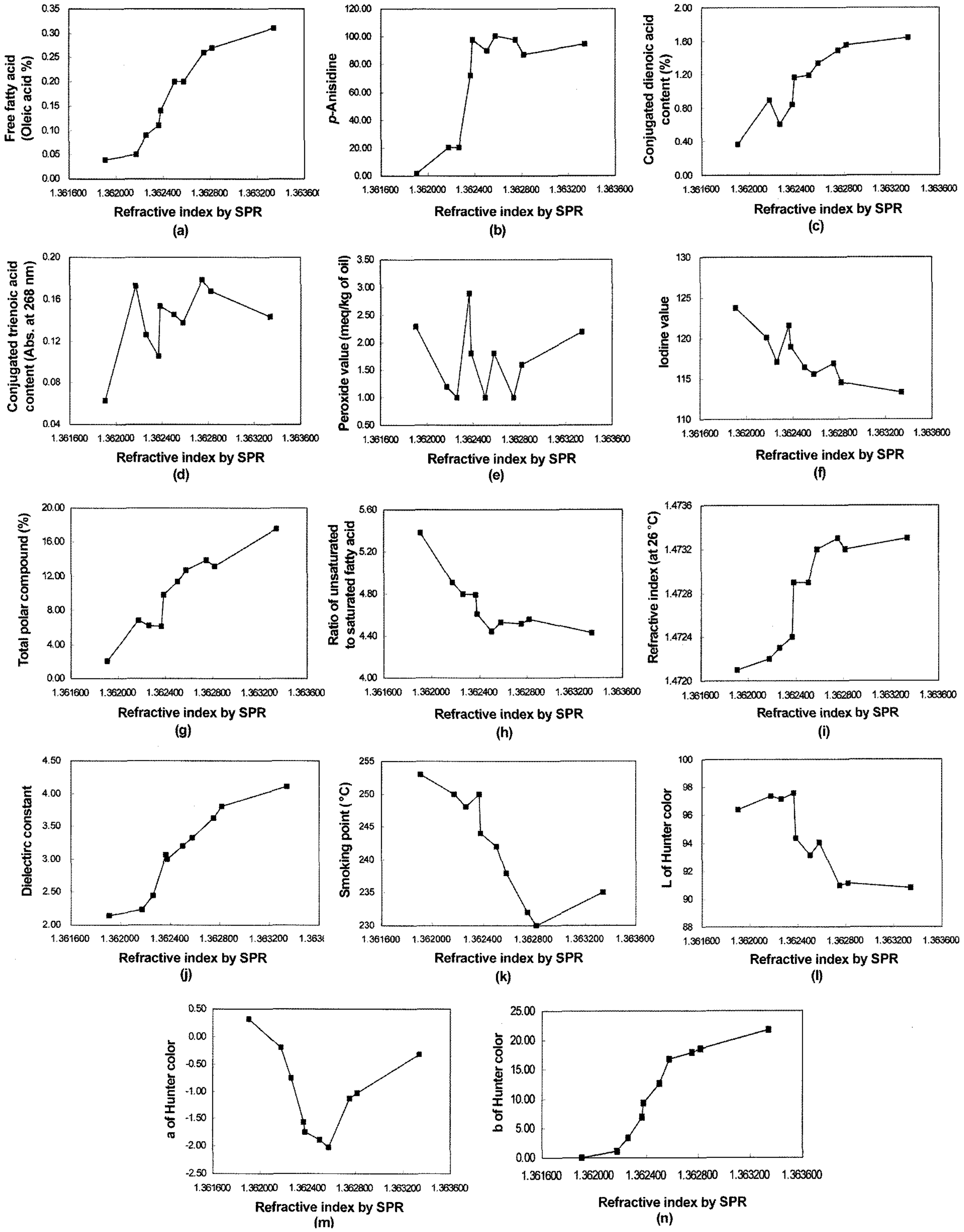

Fig. 3. Relationships of refractive index by SPR to (a) free fatty acid value, (b) *p*-anisidine value, (c) conjugated dienoic acid content, (d) conjugated trienoic acid content, (e) peroxide value, (f) iodine value, (g) total polar compound, (h) ratio of unsaturated fatty acid to saturated fatty acid, (i) refractive index, (j) dielectric constant, (k) smoking point, (l) L of Hunter color, (m) a of Hunter color, and (n) b of Hunter color.

quality of frying oil. Then, it is possible to fabricate a real-time SPR system to monitor frying oil quality. On the other hand, *p*-anisidine value, conjugated trienoic acid content, peroxide value, and a value of Hunter color showed no significant relations with the SPR refractive index at as high as 0.05 significant levels.

Table 1. Correlation coefficients and significant levels of SPR refractive index with physicochemical properties of soybean oil

Physicochemical property	Correlation coefficient	Significant probability
Free fatty acid value	0.944	0.0001***[1)]
p-Anisidine value	0.733	0.0159*
Conjugated dienoic acid content	0.900	0.0004***
Conjugated trienoic acid content	0.505	0.1367
Peroxide value	0.012	0.9736
Iodine value	-0.855	0.0016**
Total polar compound	0.948	0.0001***
Ratio of unsaturated fatty acid to saturated fatty acid	-0.800	0.0055**
Refractive index	0.856	0.0016**
Dielectric constant	0.947	0.0001***
Smoking point	-0.837	0.0025**
L of Hunter color	-0.832	0.0028**
a of Hunter color	-0.175	0.6288
b of Hunter color	0.926	0.0001***

[1)]*,**, and *** indicate the significant levels of 0.05, 0.01, and 0.001, respectively.

Table 2. The linear regression models and statistical estimates for free fatty acid value, conjugated dienoic acid content, total polar compound, dielectric constant, and b of Hunter color of soybean oil

Model : **y = a + b x** where, y and x are oil quality parameter and SPR refractive index, respectively

Oil quality parameter	Interception in model		Slope in model		Statistic for model		
	Estimate	Standard error	Estimate	Standard error	F value	Coefficient of determination	Significant probability
Free fatty acid (Oleic acid %)	-307.69	38.07	225.952	27.940	65.4	0.891	0.0001
Conjugated dienoic acid (%)	-1294.50	222.28	950.904	163.138	34.0	0.809	0.0004
TPC (%)	-15019.00	1777.18	11030.00	1304.35	71.5	0.899	0.0001
Dielectric constant	-2140.55	257.38	1573.31	188.90	69.4	0.897	0.0001
b of Hunter color	24987.00	3612.99	18347.00	2651.72	47.9	0.857	0.0001

Oil quality evaluation models with SPR parameter In this study, linear regression was used to develop simple models with SPR parameter to evaluate soybean frying oil quality. Table 2 shows the linear regression models and statistical estimates for free fatty acid value, conjugated dienoic acid content, TPC, dielectric constant, and b value of Hunter color, and their measured and predicted values are plotted in Fig. 4.

According to linear regression analyses, all models used for the prediction of free fatty acid value, conjugated dienoic acid content, TPC, dielectric constant, and b value of Hunter color of soybean oil were highly significant at 0.001 levels. In the aspect of coefficient of determination, the model TPC showed the best prediction, followed by dielectric constant, free fatty acid content, b value of Hunter color, and conjugated dienoic acid content. Both TPC and dielectric constant reflect increase in polar compounds in the frying oil. TPC by CC is recognized as the most reliable method for the prediction of frying oil quality (1), and determination of dielectric constant by FOS was developed as a rapid alternative to TPC method. However, the dielectric constant value is affected by the frying oil source and the replenishment of fresh oil (6). In addition, free fatty acid value, increased by hydrolysis of lipids during frying, has also been used as an index of frying oil quality (9). These results indicate SPR refractive index, which showed highly significant determination coefficients with main physicochemical parameters such as TPC, dielectric constant, and free fatty acid value could be used as a simple and quick method for the determination of frying oil quality.

When linear regression model was, in conclusion, used to develop the prediction model with SPR parameter for evaluating soybean frying oil quality, five physicochemical properties, free fatty acid value, conjugated dienoic acid content, dielectric constant, TPC, and b in the Hunter color system, could be described well by SPR refractive index.

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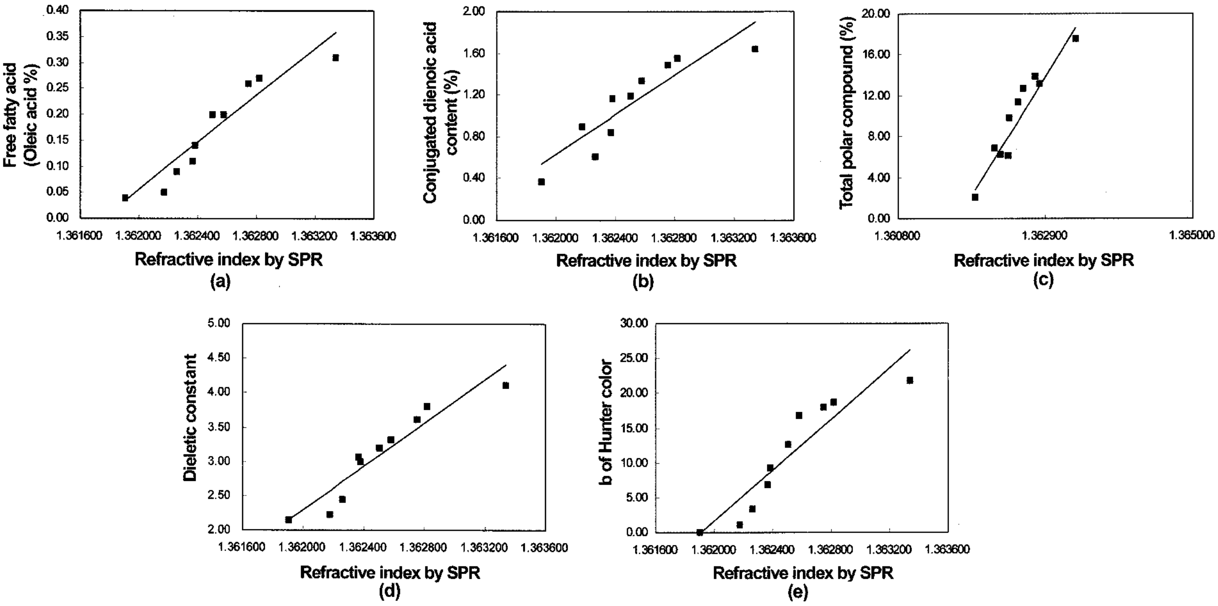

Fig. 4. The measured and predicted plots using linear regression models for (a) free fatty acid value, (b) conjugated dienoic acid content, (c) TPC, (d) dielectric constant, and (e) b of Hunter color of soybean oil.

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