Measurement of Fluorescence Polarization Angle for Characterization of Canola Oils

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Abstract *In this paper we develop simple measurement of fluorescence polarization to characterize vegetable oils, as a prospect to obtain an new test of cooking oil quality. The samples were various canola oils with relatively different their quality. The angle of fluorescence polarization and angle of linearly polarized incoming light were, respectively, measured by using two polarizer. The source of incoming light was a 532 nm green pointer laser. The profile of fluorescence polarization as a function of polarizer angle of the incoming light of each sample results two important variables, i.e. the average fluorescence polarization angle* θ_{Av} *and critical value of polarizer angle* φ_c *of the incoming light. The critical value of polarizer angle* φ_c *and* θ_{Av} *build zones of marking for canola oils and their quality.*

Keywords) — *polarization, fluorescence, canola oil quality*

I. INTRODUCTION

The change of linearly polarized light, in both of natural polarization and electro-optical effect, has been much attention in our researches for evaluation of various quality of cooking oils [1-16]. The main difference of our method from other methods is direct measurement of angle polarization through a simple pair of polarizers to characterize various vegetable and animal oils quality. The change of polarization angle, which can be obtained by transmission of light [4, 6-9, 11, 13] and fluorescence of light from samples [12, 15-16], provides a simpler tool for preliminary test of oil quality.

The main cause of transmission polarization related to the quality of various vegetable and animal oils has been studied as a consequence of the distribution and composition of saturated and unsaturated fatty acids in cooking oil [4, 8, 11]. We have found that the change of transmission polarization angle through electro-optics is a linear combination of the number of saturated and unsaturated fatty acids from the main composition in triglyceride molecules of samples [11]. Although cooking oil is an optical active sample [17], but from direct measurements using a simple pair of polarizers, the change of polarization angle of light transmissions is relatively very small (< 1°) [7], yet the polarization of light transmission can still be measured manually and shows unique polarization angles in the range 0° - 5° from different vegetable and animal oils, depending on the quality at the time of measurement. The decreasing cooking oil quality is accompanied by increasing polarization angle [4, 6-8]. In general the transmission polarization changes is independent of the angle of the incoming light polarization. Naturally, the optical activity of cooking oils is usually due to asymmetric triglycerides (TG) that can lead to the change of polarization angle. In case of transmission, assuming that most composition of oil is TG molecules, a TG molecule consisted of three fatty acids of R1R2R3, is called as asymmetry and therefore can change polarization angle if the first and third fatty acids are different R1 ≠ R3, where R2 is a fatty acid in the center of position. If R1 = R3, then the TG molecule is known as symmetry and has no contribution to the change of light polarization. In our

previous study, the change of polarization can be assigned [11] as $\theta = \theta nat + \theta elec$, where θnat is natural polarization angle due to asymmetric TG molecules, or so called as optically active TG molecules, and $\theta elec$ is electro-optics polarization angle caused by electro-optic effect due to the addition of an external electric field. The $\theta elec$ value is contributed by all TG molecules (all asymmetric and symmetric TG molecules) that become electric dipoles. In this situation, the predominant unsaturated and saturated fatty acids existed in cooking oil contribute to $\theta elec$ value. Without an external electric field, we obtain $\theta elec = 0$, and so $\theta = \theta nat$.

In case of fluorescence, the fluorescence polarization is changed against the angle of the incoming light polarization, is effectively determined by the random orientation of the molecules that make up the electric dipole due to linearly polarized incoming light [18], and is also caused by the molecular rotation motion and the energy transfer around the fluorescence molecules [19]. We have found that through the direct measurement of polarization angle, the change of fluorescence polarization, in average, is more significant and more accurate than in transmission case [16]. It can easily be measured directly through light scattered or light of fluorescence using a simple pair of polarizers [16, 20]. The direct measurement of fluorescence polarization angle in our researches is also very different from the fluorescence spectroscopy methods [21-23], which are complex and expensive apparatus, especially for an evaluation of the quality of oil directly. The change of fluorescence polarization θ is effectively dependent on the orientation of TG molecules relatively to the linearly polarized incoming light.

In this research, we measure the change of polarization angle of fluorescence light θ as a function of the change of the polarizing angle φ of the incoming light to obtain the fluorescence polarization profile on various vegetable oils. The relation between θ-value and the saturated and unsaturated fatty acids composition is also being studied assuming that the θ-value is a linear combination of number of

fatty acids according to the reference [11]. We also discuss the prospects of the method as a new alternative method for evaluation of canola oil quality.

II. MATERIALS AND METHODS

The samples were various canola oil listed in table 1. These were obtained from the market and assumed to be fulfilled by Indonesian National Standardization (SNI).

The angle of linearly polarized incoming light was adjusted by using a polarizer from φ = 0˚ to 180˚ with an increment of angle of 10˚. The change of fluorescence polarization angle θ was measured by using second polarizer (analyzer) to obtain a relation between θ-value and φ-value for all samples. To calibrate the relation between θ andφ, we measured change of polarization angle of light scattering using aqueous solution at range of polarizer angle 0° ≤ φ ≤ 180° using the experimental procedure from Firdausi et al [20]. The incoming light was pointer laser of a 532 nm-wavelength, which was perpendicular to the direction of fluorescence light. The composition of fatty acids that was assumed to influence the change of polarization was determined by using GCMS method. The simple design of the measurement of polarization angle can be described at the figure 1.

TABLE 1. Canola oils with their condition during the Measurement

Edible oil	*remark*
Canola1	-
Canola2	*Canola1 after heated in 0.5 hours*
Canola3	*Canola1 after heated in 2 hours*
Canola4	*Canola1 after heated in 4 hours*

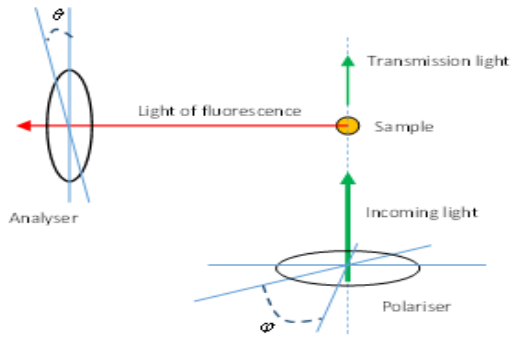

Fig. 1. The simple design of the measurement of fluorescence polarization angle θ vs. φ

III.RESULTS AND DISCUSSION

The GCMS results for vegetable oils is described in table 2 (VCO, olive, and palm oil) and table 3 (canola oil). The types of fatty acids are listed in first column and assigned by saturated, monounsaturated, and polyunsaturated fatty acids. The number of fatty acids is expressed in %. From the GCMS results, we found that the most fatty acids composition of the samples in table 2 are identical with the common composition of the fatty acids of the canola oils.

TABLE 2: the distribution of fatty acids for canola oils. The label of Canola1, Canola2 etc. are replaced by 1, 2, etc.

Fatty acids	Number of Fatty acids (%) in Canola			
	1	2	3	4
17:2	15.07	18.6		
17:0	2.97	3.53		4.36
19:2			16.33	18.19
19:1	81.96	77.87	77.51	75.65
19:0			6.16	1.8

In this section, we will discuss the dependence of θ on fatty acids composition. First we will take into account the calibration of fluorescence system using light scattering on water with the result expressed in fig 2, and second we will discuss the profile of fluorescence polarization in relation with the most fatty acids composition with the result expressed in fig 3. Figure 2 shows the calibrations result of polarization angle of light scattering using aqueous solution as function of the change of linearly polarized incoming light (polarizer angle). The minimum value θ at $\varphi = 0°$ and maximum at $\varphi = 90°$ as the consequence the choice of the polarizer axis of the incoming light in the measurement.

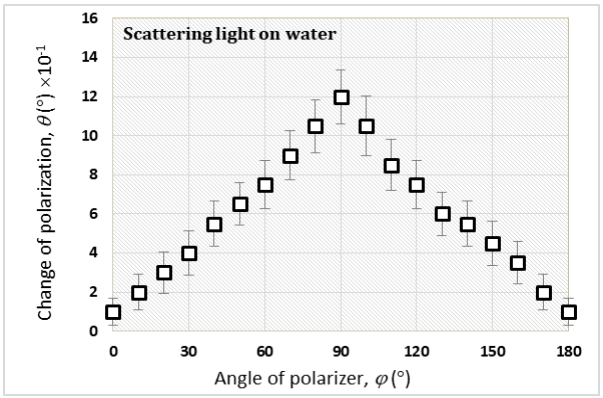

Fig.2 Calibrated polarization angle of light scattering on water in the range of polarizer angle $0° \leq \varphi \leq 180°$

The symmetrical data of θ for $0° \leq \varphi \leq 90°$ and $90° \leq \varphi \leq 180°$ indicates that the measurement apparatus' system of fluorescence polarization was well operative to conduct the data collection. The physical meaning of increasing polarizer angle φ from 0° to 90° is the variation of polarization angle of the incoming light from minimum to maximum of electric fields of light relative to the axis of analyzer. The smooth graph of polarized light scattering (θ vs. φ) shows the homogeneous small water molecules during applying linearly polarized incoming light. The change of polarization angle of light scattering on water is relative small, i.e. between 0.1° and 1.2° that gives small average value 0.58°±0.02°. This is in

agreement with our previous results [20] for scattering on water, which indicates light scattering on small individual water molecules.

The symmetrical graphs of fluorescence polarization works also for θ as function of φ. Figure 3 shows the profile of fluorescence polarization angle in the range $0 \le \varphi \le 180°$ of each sample in left side and its GCMS result in right side. The profile of fluorescence polarization angle in fig 3. All profiles of fluorescence polarization angle of vegetable oil show symmetrical characteristics in the range $0 \le \varphi \le 180°$, i.e. the polarization in the range $0 \le \varphi \le 90°$ is reflected with identical values in the range $90° \le \varphi \le 180°$.

Although the values are similar, but there are still some different characteristics of the change of polarization θ. From the profile shown in fig 3, we found the following results:

1. First, θ has different value at $\varphi = 0°$ and $\varphi = 90°$ in each vegetable oil, which results different average polarization angle θ_{Av} in the interval $0 \le \varphi \le 180°$.
2. Second, θ has different minimum value at critical polarizer angle φ_c.
3. Third, actually the critical value φ_c is also different for certain oils.

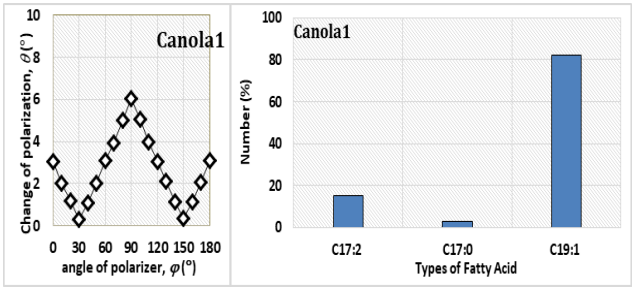

Fig. 3 profile of fluorescence polarization change as function of polarization angle of incoming light for Canola1.

According to the profile of fluorescence polarization angle, we obtained some characteristics values for the various sample condition, i.e. the θ values at $\varphi = 0°$ and $\varphi = 90°$, θ_{min} at critical polarization value $\varphi = \varphi_c$, and average value θ_{Av} listed in table 4.

TABLE 3: θ-value of light of fluorescence at $\varphi = 0°$ and 90°, and critical polarization angle φ_c of incoming light

Edible oil	θ(°)		φ_c (°)	θ_{Av}(°)
	$\varphi = 0°$	$\varphi = 90°$		
Canola1	2.90 ± 0.16	6.15 ± 0.08	30	2.58
Canola2	3.10 ± 0.14	6.25 ± 0.12	30	2.71
Canola3	3.25 ± 0.14	6.40 ± 0.15	30	2.83
Canola4	3.45 ± 0.15	6.70 ± 0.13	30	3.05

Considering the results above, the critical value φ_c and average value θ_{Av} seem to play very important roles for fluorescence polarization of each sample. The critical value φ_c shows reversing phase of the direction of electric fields at that point. We found, in the experiment, that the phase of transformation of θ from left circular rotation when φ changes from 0° to φ_c, and the right circular rotation when φ increases gradually from φ_c to 90°. Normally, in light scattering of water or sugar solution with low concentration, the minimum change of polarization angle occurs at $\varphi = 0°$ [20]. In our case, the minimum fluorescence polarization shifts from $\varphi = 0°$ to critical angle φ_c, which shows at least different orientation of TG molecules during exposed by the light. The depolarized light of fluorescence and the reversed phase at φ_c are caused also by dynamical orientation or vibration of molecules during transfer of energy from incoming light λ to light of fluorescence λ_f. Through fluorescence polarization, the orientation of molecules and dynamical molecular rotation or vibration are shown by characteristics pattern of polarization angle dependent on the homogeneous level or most dominant composition of TG molecules in each canola oil.

In the other hand, Canola1 shows smallest θ_{Av} and highest value $\varphi_c = 30°$ from others. The distribution of the fatty acids in Canola1 was dominated by monounsaturated fats 19:1 more than 80% in TG molecules. This results in high symmetrical TG of three identical monounsaturated fatty acids of $R_2R_2R_2$, which leads small θ_{Av}. We proposed that the smooth curves θ vs. φ for Canola1 indicates that the monounsaturated fatty acids were dominated by trans fats 19:1.

The relation of fluorescence polarization as linear combination of fatty acids in can be found easier by using the fatty acids composition in Canola1, Canola2, Canola3,and Canola4 that leads to only 4 linear equations to be solved. There are 4 different fatty acids with different number of composition and 4 different θ_{Av}, which will give 4 different linear equations and can be arranged as follows (table 4).

TABLE 4 : θ_{Av} and the fatty acids number (%) of Canola

Edible oil	N_1	N_2	N_3	N_4	N_5	θ_{Av} (°)
	17:2	17:0	19:2	19:1	19:0	
Canola1	15.07	2.97	0	81.96	0	2.58
Canola2	18.60	3.53	0	77.81	0	2.71
Canola3	0	0	16.33	77.51	6.16	2.83
Canola4	0	4.36	18.19	75.65	1.8	3.05

The variables N_1, ..., N_5 represent the number (%) of fatty acids of 17:2, ..., 21:0, respectively. From the table we have a linear equation as follows

$$a_1N_1 + a_2N_2 + a_3N_3 + a_4N_4 + a_5N_5 + a_6N_6 = \theta_{Av} \quad (1)$$

where the coefficients of a_1, ..., a_6 are respectively related to the fatty acids of 17:2, ..., 21:0. It measures, how influenced the fatty acids to θ_{Av} is. By inserting the variables N_i from

table 4 into the equation (1), we found the coefficient a_i written in the last row of table 5.

TABLE 5: the coefficient a_i of the fatty acids in Canola

a_1 (17:2)	a_2 (17:0)	a_3 (19:2)	a_4 (19:1)	a_5 (19:0)	a_6 (21:0)
–0.24	1.84	–0.47	0.01	1.59	2.31

The positive coefficients shown in table 5 indicates that the fluorescence polarization positively dependent on long chain of the saturated fatty acids. The higher the saturated fats, so increases the fluorescence polarization angle. The negative sign of the coefficients indicates that the increasing polyunsaturated fats, decreases the fluorescence polarization. This patterns has been already investigated and proposed in case of transmission polarization [11]. So we have proven that the angle of fluorescence polarization is also a linear combination of the fatty acids composition.

In this following part, we discuss the possibilities the fluorescence polarization as a new alternative method for evaluation of canola oil quality. From table 3 we found that various types of oil have their characteristics and provide to differentiate the types and their quality. There are some possibilities to differentiate the various canola oils.

IV. CONCLUSION

The profile of fluorescence polarization as a function of polarizer angle of the incoming light of each sample provides two important variables, i.e. the average fluorescence polarization angle θ_{Av} and critical value of polarizer angle φ_c of the incoming light. The average of polarization angle is a linear combination of the number of most fatty acids composition. The average of angle θ_{Av} increases with increasing the saturated fats, and decreases with increasing polyunsaturated fats. The critical value of polarizer angle φ_c and θ_{Av} build zones of marking for various types of canola oils and their quality. The simple measurement of fluorescence polarization angle seems powerful for fast preliminary test of canola oil quality .

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