

IODINE VALUES ESTIMATION OF VEGETABLE OILS BY FTIR SPECTROSCOPY

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Key words: FTIR, iodine value, vegetable oils

A rapid and simple method for the estimation of the iodine values (IV) of vegetable oils by FTIR spectroscopy was developed and tested. Iodine values of 12 edible oils from local supermarket were measured by thiosulfate titration and correlated with spectral data from FTIR. The absorbance values of carbon-carbon double bond at 1654 cm^{-1} ($A_{C=C}$) and carbonyl group ($A_{C=O}$) at 1746 cm^{-1} and 3470 cm^{-1} were correlated with IV. The intensities of the carbon-carbon double bond fundamental and the carbonyl group overtone absorption bands provide the best linear regressions $IV = 63.37 \times A_{C=C} / A_{C=O} - 29.5$; $R = 0.956$.

INTRODUCTION

Iodine values (IV) as a very important indicator of total unsaturation of fats and oils have been measured by thiosulfate titration assay [EN ISO 3961, 1999], chromatographic methodologies, Fourier transform infrared (FTIR), near infrared and Raman spectrometry [Thin Sue Tang, 2001]. Of these the FTIR and FTNIR spectroscopy together with multivariate statistical methods [Hendl *et al.*, 2001; Cox *et al.*, 2000] is the rapid way for determination of IV with high accuracy. The purpose of this paper was to evaluate the use of FTIR and linear correlation procedure for the estimation of IV.

MATERIALS AND METHODS

Twelve edible oils were collected from local supermarket. The iodine values of these oils were measured by thiosulfate titration assay [EN ISO 3961, 1999]. Spectroscopic analysis of oils was carried out using the Perkin Elmer SPECTRUM RX 1 and a standard NaCl cavity cell with a path length of 0.05 mm and standard cell holder. A small amount of each sample without additional preparation was placed in the clean cavity cell. Each sample was scanned 16 times. For any oil at least two separate spectra were scanned.

RESULTS AND DISCUSSION

Carbon-carbon double bond absorption band appears in the FTIR spectra at 1654 cm^{-1} and is strongly overlapped by intensive carbonyl absorption band at 1746 cm^{-1} (Figure 1). The strong overlapping effects and differences in intensities reduce the use of band at 1654 cm^{-1} .

To ascertain the better way to calculate the correct height of the peak in absorbance one uses three different Perkin Elmer SPECTRUM RX 1 routine peak height calculation

operations: from horizontal axis (automatical, Aut) and from horizontal baseline through the lower point left and right from the peak (left, Le and right, Ri). Acquired three different series of bands intensities $A_{C=C}$ Aut, $A_{C=C}$ Le and $A_{C=C}$ Ri from three independent measurements for any oil are listed in Table 1.

The standard deviation (SD) of the results is about 5% for absorbance measurement by “automatical” and “left” mode and about 4% by “right” mode. According to Hendl *et al.* [2001], the SD 5% level is good enough for the determination of IV by FTIR. The calculated $A_{C=C}$ correlate (Table 1, R – coefficients of correlation, calculated by program Correl) with chemically determined IV, but only by the use of the $A_{C=C}$ Ri the correlation coefficient slightly exceeds 0.9. According to Hendl *et al.* [2001], a better correlation cannot be anticipated because the $A_{C=C}$ values include information only about the carbon-carbon double bond concentration [C=C], but IV is a complex characteristic including information about [C=C] and triglyceride [trig] concentration. As the [trig] is concerned to carbonyl group concentration [C=O] and triglyceride molecular weight (MW), better correlation [Hendl *et al.*, 2001] between IV and [C=C]/[C=O] is given by:

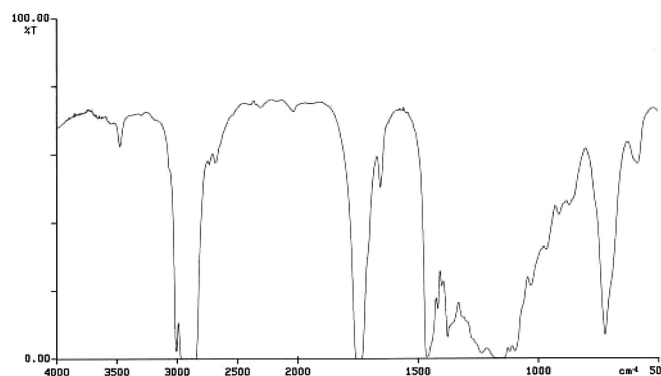


FIGURE 1. Infrared absorbance spectrum of oil Nr 3.

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$$IV = g I_2 / 100 \text{ g oil} = k_1 \times [C=C] / [\text{trig}] = k_2 \times [C=C] / [C=O] \times 1/MW$$

In agreement with Beer's Law, one can obtain the following equation:

$$IV = k \times A_{C=C} / A_{C=O} \times 1/MW.$$

Mean values of three separate measurements of carbonyl group fundamental band intensity at 1746 cm^{-1} ($A_{C=O}$ Aut, $A_{C=O}$ Le and $A_{C=O}$ Ri) and overtone band intensity at 3470 cm^{-1} ($A_{C=O}$ OAut, $A_{C=O}$ OLe and $A_{C=O}$ ORi) are listed in Table 2.

The coefficients of linear correlation between $A_{C=O}$ Aut and $A_{C=O}$ Le, $A_{C=O}$ Ri, $A_{C=O}$ OAut, $A_{C=O}$ OLe, $A_{C=O}$ ORi and

TABLE 1. Average experimental C=C absorption band intensities at 1654 cm^{-1} .

No.	Iodine value	$A_{C=C}$ Aut	$A_{C=C}$ Le	$A_{C=C}$ Ri
1.	80.29	0.288	0.064	0.154
2.	99.55	0.368	0.081	0.201
3.	106.87	0.469	0.117	0.269
4.	115.45	0.455	0.111	0.255
5.	124.4	0.41	0.093	0.243
6.	128.93	0.44	0.104	0.25
7.	130.8	0.41	0.097	0.245
8.	130.93	0.44	0.107	0.266
9.	145.89	0.437	0.11	0.272
10.	153.68	0.451	0.117	0.285
11.	170.87	0.578	0.156	0.378
12.	184.3	0.538	0.144	0.362
	SD (%)	5.2	4.7	4.3
	R	0.841	0.865	0.921

TABLE 2. Average experimental C=O absorption band intensities at 1746 cm^{-1} and 3470 cm^{-1} .

No.	$A_{C=O}$ Aut	$A_{C=O}$ Le	$A_{C=O}$ Ri	$A_{C=O}$ OAut	$A_{C=O}$ OLe	$A_{C=O}$ ORi
1.	3.081	2.966	2.858	0.204	0.096	0.091
2.	3.22	3.08	2.934	0.22	0.101	0.098
3.	3.297	3.122	2.944	0.27	0.115	0.102
4.	3.1	2.98	2.86	0.215	0.108	0.096
5.	3.112	2.993	2.855	0.206	0.098	0.089
6.	3.225	3.063	2.86	0.213	0.098	0.092
7.	3.226	3.084	2.918	0.212	0.094	0.086
8.	3.228	3.09	2.924	0.208	0.098	0.9
9.	3.206	3.07	2.893	0.226	0.107	0.105
10.	3.236	3.091	2.905	0.23	0.096	0.086
11.	3.463	3.279	3.019	0.282	0.127	0.112
12.	3.329	3.171	2.935	0.225	0.111	0.101
Average	3.227	3.082	2.909	0.204	0.104	0.163
	R	0.995	0.916	0.804	0.74	0.03
				R	0.86	0.02

those between $A_{C=O}$ OAut and $A_{C=O}$ OLe, $A_{C=O}$ ORi are listed in Table 2. As shown there is only one good correlation between $A_{C=O}$ Aut and $A_{C=O}$ Le, indicating that only $A_{C=O}$ Aut or $A_{C=O}$ Le are useful for IV calculation.

Average overtone C=O band intensities are close to the average C=C band intensities and its division will give more sensitive function for IV calculation, accordingly $IV = k \times A_{C=C} / A_{C=O}$ than the division of C=C band intensities by C=O fundamental band intensities. As shown in Table 3, improvement can be observed and there is correlation with $R = 0.956$.

The best equations for calculation of the IV are:

$$IV = 128.37 A_{C=C} \text{ Ri} / A_{C=O} \text{ OAut} - 19.09 \quad (1)$$

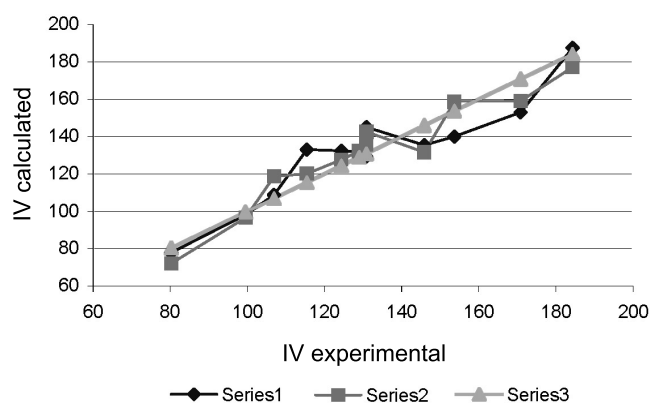
$$IV = 63.37 A_{C=C} \text{ Ri} / A_{C=O} \text{ OLe} - 29.5 \quad (2)$$

The calculated and chemically determined iodine values are shown in Figure 2.

Evidently for a precise determination of IV, the conformity of experimental and calculated values is not good enough and equation 2 may be used only for a rapid estimation of IV. Insufficiently good correlation of the calculated and experimental values indicates that the calculations of the heights of the peaks in absorbance include some deviations, requiring additional calibration prior to every series of analyses with a set of standards or multivariate calibration procedure [Hendl *et al.*, 2001]. Without additional procedures even if the best equation (2) is used, the confidence interval will be better than 10 only by taking into account three separate experimental values without significant systematic errors. The later betterment by consideration of MW values request additional determination of saponification number and can give a very little progress because classical vegetable oils such as sunflower, olive, peanut, and rapeseed (low erucic) [Bondioli, 2001].

TABLE 3. Iodine values and $A_{C=C} / A_{C=O}$ coefficients of correlation.

Divider	$A_{C=C}$ Aut	$A_{C=C}$ Le	$A_{C=C}$ Ri
1.0	0.841	0.865	0.921
$A_{C=O}$ Aut	0.828	0.866	0.93
$A_{C=O}$ Le	0.826	0.863	0.927
$A_{C=O}$ Ri	0.844	0.872	0.931
$A_{C=O}$ OAut	0.807	0.909	0.934
$A_{C=O}$ OLe	0.852	0.922	0.956
$A_{C=O}$ ORi	0.383	0.524	0.58

FIGURE 2. Comparison of calculated and chemically determined iodine values. Series 3 is imitation line $R=1$.

SUMMARY

The use of FTIR application for estimation of iodine values (IV) using standard EXCEL calculations was assessed by 12 edible oils from local supermarket. Carbon-carbon double bond absorption band that appears in the FTIR spectrum at 1654 cm^{-1} is strongly overlapped by intensive carbonyl absorption band at 1746 cm^{-1} (Figure 1). To ascertain the better way to calculate the correct height of the peak in absorbance one can use three different Perkin Elmer SPECTRUM RX 1 routine peak height calculation operations: from horizontal axis (automatic, Aut) and from horizontal baseline through the lower point left and

right from the peak (left, Le and right, Ri). The three different series of bands intensities acquired $A_{C=C}$ Aut, $A_{C=C}$ Le and $A_{C=C}$ Ri from three independent measurements for any oil are listed in Table 1. Calculated $A_{C=C}$ correlate (Table 1, R – coefficients of correlation, calculated by program Correl) with chemically determined IV, but only by the use of the $A_{C=C}$ Ri the correlation coefficient slightly exceeds 0.9. The improvement of the correlations of spectral data with chemically determined IV is reached by the use of the information about the carbonyl group absorbance (Table 2) and the best equation ($R=0.96$) for the estimation of IV (Table 3) was:

$$IV = 63.37 A_{C=C} Ri / A_{C=O} OLe - 29.5$$

where $A_{C=O} OLe$ is the carbonyl group overtone absorbance at 3470 cm^{-1} , determined by the procedure “left”. For a precise determination of IV, the conformity of the experimental and calculated values (Figure 2) is not good enough and equation may be used only for a rapid estimation of iodine values.

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