

Relationships between the Composition of Edible Oils and Lard and the Ratio of the Absorbance of Specific Bands of Their Fourier Transform Infrared Spectra. Role of Some Bands of the Fingerprint Region

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Sixteen samples of edible oils and lard have been studied by means of Fourier transform infrared spectroscopy. The spectra were recorded from a film of pure oil or lard between two disks of KBr. The height and the area of the bands were measured taking two baselines. Ratios between the absorbances of the bands and the correlation matrix of these data were calculated. Some ratios between absorbances contain similar information. The iodine value of the samples was also determined according to the classical iodometric method, and very close relationships were found between this parameter and the ratios of absorbance of some bands. The direct use of some of the absorbance ratios as characteristic parameters of edible oils and fats is proposed. In addition, ratios of absorbance of specific bands, some of them of the fingerprint region, have been found to be highly dependent on the sample composition. Equations obtained from ratios of absorbances and composition data are valuable in the prediction of the proportion of saturated, monounsaturated, and polyunsaturated acyl groups in oils and lard. The importance of the absorbance of some specific bands of the fingerprint region of the infrared spectra to characterize edible oils and fats has been shown for the first time.

Keywords: *Edible oils; lard; characterization; Fourier transform infrared spectroscopy; fingerprint region; absorbance; iodine value; monounsaturated; saturated; polyunsaturated; acyl groups*

INTRODUCTION

Infrared spectroscopy has scarcely been used in the study of edible oils and fats in the past (Guillén and Cabo, 1997a). However, with the incorporation of the Fourier transform technique, its use is increasing. The absorbances of the bands of the infrared spectra at 968 cm^{-1} and at 1711 cm^{-1} have been used to estimate the trans double bonds (IUPAC, 1987; AOCS, 1989; Kaufman et al., 1959; Lanser and Emken, 1988; Belton et al., 1988; Sleeter and Matlock, 1989; Ulberth and Haider, 1992; Van de Voort et al., 1995; Mossoba et al., 1996; Ratnayake and Pelletier, 1996) and the free fatty acid content (Lanser et al., 1991; Ismail et al., 1993), respectively.

Likewise, the degree of unsaturation of edible oils and fats has been related to the intensity of specific bands. Pioneers studies (Sinclair et al., 1952) have shown the existence of close relationships between the number of double bonds in mixtures of cis fatty acids (oleic, linoleic, araquidonic) and the ratio between the absorbance of the stretching vibration band of the $-\text{CH}_2-$ groups, at 2920 cm^{-1} , and the difference between the absorbance of this band and that at 3020 cm^{-1} due to the stretching vibration band of the $=\text{CH}-$ cis group; high (low) values of this ratio indicate high (low) unsaturation in the sample subject of study.

Other authors have found close relationships between the iodine value (IV) of edible oils and either the

absorbance of the band at 3007 cm^{-1} (stretching vibration of the $=\text{CH}-$ cis group) (Muniategui et al., 1992) or the absorbance of the band at 1658 cm^{-1} due to the stretching vibration of the $-\text{C}=\text{C}-$ cis group (Bernard and Sims, 1980). Similar relationships have been found between the IV and the ratio between the absorbances of the band at $\approx 3006 \text{ cm}^{-1}$ ($=\text{CH}-$ cis group) and of the band at 2857 cm^{-1} (Arnold and Hartung, 1971) or at 2854 cm^{-1} (Afran and Newbery, 1991), due to the symmetric stretching vibration of the $-\text{CH}_2-$ group.

From the above-mentioned, it can be observed that information from only six specific bands has been used and related to the characteristics of the oil samples. However, the recently used partial least-squares analyses (Van de Voort et al., 1992, 1994, 1995) applied to the study of infrared spectra of oils and fats also use the fingerprint region of the spectra, without specification of the bands of interest.

In a previous paper we studied the relationships between frequency data of all bands of the Fourier transform infrared spectra, of edible oils and fats, and the composition of the sample, and close relationships were found to exist between the frequency of some specific bands of the fingerprint region and the proportion of monounsaturated or saturated acyl groups in the sample (Guillén and Cabo, 1997b).

In this paper, ratios between the absorbance of all bands in the infrared spectra of several oils and lard are determined to discover if any of them could be used as a characteristic parameter of the sample; to test this possibility, relationships between these values and the

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Table 1. Composition of the Samples Given by the Producers Together with the Iodine Value and Its Standard Deviation (SD)

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
polyunsaturated acyl groups ^a (%)	10		14	8		8			57	59	64	60				
saturated acyl groups ^a (%)	40.5		14	13		13			13	13	12	13				
monounsaturated acyl groups ^a (%)	47.5		71	79		79			30	27	24	27				
iodine value (g of I ₂ /100 g of oil)	61.0	84.6	83.0	84.8	83.3	83.3	107.8	124.1	130.0	131.8	131.8	131.6	135.1	131.5	134.1	131.9
SD	±0.0	±0.2	±0.5	±0.7	±0.4	±0.3	±0.8	±0.8	±0.8	±0.8	±0.8	±1.5	±0.7	±1.6	±0.8	±0.6

^a Percentage (%) by weight of polyunsaturated, saturated, and monounsaturated acyl groups was determined by gas chromatography.

IV are studied. In addition, relationships between the above-cited ratios and the composition of the samples expressed as percentage of saturated, monounsaturated, and polyunsaturated acyl groups are also studied to determine if it is possible to deduce the composition of oils and fats in terms of their main components from the Fourier transform infrared spectra. This study will allow one to know which bands, including those of the fingerprint region, are important to characterize edible oils and fats. Ratios between absorbance values, instead of absolute absorbance values, are used, because, in the former, all variable circumstances involved in the sample preparation and registration of each spectra are eliminated.

EXPERIMENTAL PROCEDURES

Samples. Sixteen lipid-rich commercial products were obtained from local supermarkets or from producers. All are very commonly used in the Spanish diet, except sesame oil. The sample collection includes the following: one solid sample of lard, named A; two samples of extra virgin olive oil, designated B and C; three samples of olive oil made of a mixture of refined and virgin olive oil, named D–F; one sample of virgin sesame oil, G; one sample of seed oil of unknown vegetable origin, designated H; two samples of refined corn seed oil, I and J; a mixture of sunflower and corn oils, K; four samples of refined sunflower oil, L–O; and, finally, one sample of refined soybean oil, P. The percentage by weight of polyunsaturated, saturated, and monounsaturated acyl groups of samples A, C, D, F, and I–L was determined by the producers according to the gas chromatographic method of the Association of Official Analytical Chemists (AOAC, 1990).

Fourier Transform Infrared Spectra. The infrared spectra were recorded with a Fourier transform infrared spectrometer Nicolet Magna-IR 550 spectrometer (Nicolet Instrument Corp., Madison, WI), interfaced to a 486 personal computer operating under Windows-based Nicolet Omnic software (version 3.1). The instrument was purged with a Balston dryer (Balston, Lexington, MA) to minimize water vapor and CO₂ interferences.

Spectral Acquisition. A film of a small amount of each sample (≈2 μL for liquids) was deposited between two disks of KBr, avoiding the presence of air, as in previous studies (Guillén and Cabo, 1997b). Multiple spectra (between three and four) were collected from each sample over different periods of time. All spectra were recorded from 4000 to 500 cm⁻¹ with a resolution of 4 cm⁻¹. For each spectrum 32 interferograms were co-added before Fourier transformation and zero-filled to give a data point spacing of ≈1.9 cm⁻¹.

Study of the Spectra. The height of each band was measured automatically by means of a macro program taking two baselines: 3600–2472 and 1900–530 cm⁻¹. The same procedure was used to determine the band areas. This procedure avoids the experimental errors associated with the subjectivity of the external operators.

Iodine Value. This was determined by means of the AOAC method (AOAC, 1990).

RESULTS AND DISCUSSION

The edible oils and the lard are constituted basically of triacylglycerols of various fatty acids esterified to glycerol with different substitution patterns, lengths, and degrees of unsaturation of the chains and of other minor components; Table 1 shows the fatty acid composition of some of these samples, given by the producers.

In Figure 1 only the spectra of some of the studied oils are given. The great similarity between the spectra of the several samples can be observed. However, differences in the frequency and in the intensity of the bands are evident. The approximate frequency of all bands or shoulders and its tentative assignment to the several modes of vibration of the functional groups present in the sample, together with their approximate intensity, are given in Table 2, although it should be pointed out that the assignment of the bands in some cases is difficult, especially in the fingerprint region, because generally the bands are due to more than one single functional group. The higher differences between spectra of several samples due to the intensity of bands, observable with the naked eye, are in absorptions at approximately 3006 cm⁻¹ (band c), 1654 cm⁻¹ (band k), 1417 cm⁻¹ (band n), 1402 cm⁻¹ (band o), 1238 cm⁻¹ (band r), 1163 cm⁻¹ (band s), 1118 cm⁻¹ (band t), 1097 cm⁻¹ (band u), 914 cm⁻¹ (band y), and 723 cm⁻¹ (band z).

The Beer–Lambert law relates the observed absorbance (*A*) of a given band and the concentration (*c*) of the functional group that causes this band through the equation $A = \epsilon bc$, where ϵ is the absorption coefficient characteristic of each functional group and *b* is the sample thickness. Table 3 gives some of the calculated ratios between absorbances of the different bands in Table 2, determined by means of the height of the bands. Taking into account all of the above-mentioned, ratios of absorbances, in Table 3, represent ratios between the concentrations of the corresponding functional groups multiplied by a constant factor, the same for all samples, which is dependent on the two functional groups involved in each ratio. That is to say, these ratios are proportional to the concentrations of the corresponding functional groups in each sample, with the same proportionality constant in all cases. Obviously, ratios of bands due to more than one single functional group are related to all functional groups involved in each absorption.

Although only some ratios are given in Table 3, all of those mathematically possible were calculated, regardless of their physicochemical significance, and the matrix correlation between these data was calculated to determine which of these values have similar or

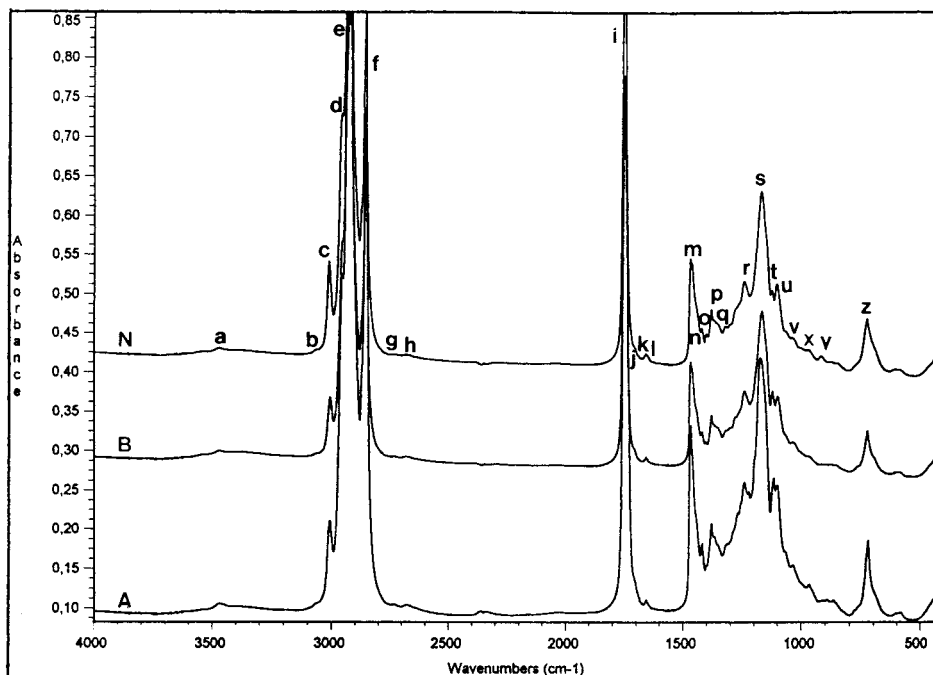


Figure 1. Fourier transform infrared spectra of lard, A, extra virgin olive oil, B, and sunflower oil, N.

Table 2. Frequencies (in cm^{-1}) of Bands (b) or Shoulders (s) of Some Edible Oils and Lard Mid-Infrared Spectra, Together with the Tentatively Assigned Functional Group, the Mode of Vibration, and the Approximate Intensity

band	frequency	functional group	mode of vibration	intensity ^a
a	3468 (b)	-C=O (ester)	overtone	w
b	3025 (s)	=C-H (trans)	stretching	vw
c	3006 (b)	=C-H (cis)	stretching	m
d	2953 (s)	-C-H (CH ₃)	stretching (asym)	m
e	2924 (b)	-C-H (CH ₂)	stretching (asym)	vst
f	2853 (b)	-C-H (CH ₂)	stretching (sym)	vst
g	2730 (b)	-C=O (ester)	Fermi resonance	vw
h	2678 (b)	-C=O (ester)	Fermi resonance	vw
i	1746 (b)	-C=O (ester)	stretching	vst
j	1711 (s)	-C=O (acid)	stretching	vw
k	1654 (b)	-C=C- (cis)	stretching	vw
l	1648 (b)	-C=C- (cis)	stretching	vw
m	1465 (b)	-C-H (CH ₂ , CH ₃)	bending (scissoring)	m
n	1417 (b)	=C-H (cis)	bending (rocking)	w
o	1400 (b)		bending	w
p	1377 (b)	-C-H (CH ₃)	bending (sym)	m
q	1319 (b, s)		bending	vw
r	1238 (b)	-C-O, -CH ₂ -	stretching, bending	m
s	1163 (b)	-C-O, -CH ₂ -	stretching, bending	st
t	1118 (b)	-C-O	stretching	m
u	1097 (b)	-C-O	stretching	m
v	1033 (s)	-C-O	stretching	vw
x	968 (b)	-HC=CH- (trans)	bending out of plane	w
y	914 (b)	-HC=CH- (cis) ?	bending out of plane	vw
z	723 (b)	-(CH ₂) _n -, -HC=CH- (cis)	rocking, bending out	m

^a vst, very strong; st, strong; m, medium; w, weak; vw, very weak.

related information. In Table 4 the correlation matrix of some of these ratios is given. It can be expected that ratios between bands due to =CH- cis groups and bands due to -CH₂- groups, such as A_e/A_c , A_c/A_f , A_c/A_m , or A_f/A_z , contain similar information, and this is confirmed in the matrix correlation with correlation coefficients very close to 1; these four series of parameters give information on the degree of saturation or unsaturation of each sample because the trans double bonds content is low in edible oils and fats. There can be observed in Table 3 different values, of the above-cited ratios, for lard, olive oil, sesame oil, and unknown seed oil; sunflower, soybean, and corn oils show similar values, different from the former. This fact is due to

the sunflower, corn, and soybean oils here studied having similar degrees of unsaturation.

On the other hand, ratios between absorbances of bands due to vibrations of the -COO- group of the triglyceride esters and bands of -CH₂- or =CH- cis groups, in the strict sense, give values proportional to the concentration of these functional groups in each sample with the same proportionality constant for all samples and so are useful values in comparative studies. In addition, there is a close correlation between these ratios and those ratios that relate -CH₂- groups and =CH- cis groups. That is to say, ratios between the absorbance of bands of the triglyceride esters and the absorbance of bands either of =CH- cis groups or

Table 3. Ratios between Absorbances of Some Bands of the Infrared Spectra Together with Their Standard Deviation

sample	A_c/A_e^a	A_c/A_f^a	A_c/A_m^a	A_f/A_z	A_c/A_i^a	A_c/A_s^a	A_f/A_u^b	A_f/A_n	A_f/A_u^b
A	8.01 ± 0.00	12.93 ± 0.00	47.21 ± 0.00	8.88 ± 0.07	13.82 ± 0.04	33.36 ± 0.39	10.66 ± 0.06	10.49 ± 0.12	54.45 ± 0.72
B	10.39 ± 0.26	17.44 ± 0.23	59.35 ± 0.47	8.35 ± 0.28	15.83 ± 0.19	39.13 ± 0.24	10.74 ± 0.12	9.88 ± 0.52	47.91 ± 1.13
C	10.31 ± 0.17	17.32 ± 0.21	59.70 ± 0.99	8.37 ± 0.07	15.65 ± 0.20	39.19 ± 0.63	10.81 ± 0.08	10.19 ± 0.16	48.91 ± 0.55
D	10.51 ± 0.07	17.55 ± 0.12	60.33 ± 0.18	8.20 ± 0.04	15.79 ± 0.12	39.61 ± 0.25	10.89 ± 0.03	10.37 ± 0.10	49.87 ± 0.39
E	10.51 ± 0.36	17.56 ± 0.34	59.60 ± 1.36	8.36 ± 0.20	15.95 ± 0.35	39.65 ± 0.64	10.78 ± 0.10	9.92 ± 0.55	48.67 ± 1.15
F	10.37 ± 0.38	17.39 ± 0.48	59.83 ± 0.57	8.44 ± 0.17	15.65 ± 0.43	39.22 ± 0.14	10.87 ± 0.02	10.34 ± 0.82	49.52 ± 3.20
G	14.02 ± 0.14	23.56 ± 0.28	76.24 ± 1.04	6.98 ± 0.04	19.46 ± 0.27	48.27 ± 0.48	9.70 ± 0.03	9.12 ± 0.47	42.26 ± 1.66
H	15.57 ± 0.25	26.38 ± 0.24	84.53 ± 0.65	6.40 ± 0.11	20.39 ± 0.37	51.84 ± 0.43	9.57 ± 0.02	8.62 ± 0.09	41.10 ± 0.49
I	16.81 ± 0.58	28.01 ± 0.31	87.92 ± 0.32	6.16 ± 0.03	21.47 ± 0.38	53.63 ± 0.24	9.34 ± 0.01	8.49 ± 0.05	39.62 ± 0.14
J	16.62 ± 0.27	28.07 ± 0.34	87.81 ± 0.60	6.25 ± 0.07	21.49 ± 0.20	53.49 ± 0.41	9.35 ± 0.02	8.33 ± 0.05	38.87 ± 0.63
K	16.82 ± 0.21	28.62 ± 0.23	89.24 ± 1.30	6.13 ± 0.03	21.55 ± 0.31	54.30 ± 0.48	9.29 ± 0.00	8.16 ± 0.41	38.50 ± 1.42
L	16.93 ± 0.18	28.71 ± 0.13	90.22 ± 0.95	6.10 ± 0.12	21.64 ± 0.17	54.57 ± 0.60	9.24 ± 0.02	8.48 ± 0.17	38.95 ± 0.72
M	17.49 ± 0.12	29.71 ± 0.14	92.90 ± 0.24	5.96 ± 0.04	22.08 ± 0.19	56.00 ± 0.19	9.19 ± 0.02	8.37 ± 0.11	38.58 ± 0.38
N	16.61 ± 0.25	27.98 ± 0.13	87.48 ± 0.73	6.19 ± 0.06	21.31 ± 0.05	53.68 ± 0.10	9.29 ± 0.02	8.36 ± 0.19	38.58 ± 0.45
O	17.65 ± 0.32	29.67 ± 0.31	93.63 ± 0.05	6.00 ± 0.04	22.25 ± 0.41	56.37 ± 0.37	9.18 ± 0.02	8.58 ± 0.12	39.30 ± 0.55
P	17.20 ± 0.20	29.06 ± 0.19	93.46 ± 0.12	6.03 ± 0.03	21.23 ± 0.33	55.40 ± 0.27	9.20 ± 0.06	8.68 ± 0.12	40.06 ± 0.41

^a Ratio values multiplied by 10². ^b Ratio values multiplied by 10.

Table 4. Correlation Matrix of the Ratios of Absorbances of Specific Bands of the Infrared Spectra

ratio	A_c/A_e	A_c/A_f	A_c/A_m	A_f/A_z	A_c/A_i	A_c/A_s
A_c/A_e	1.0000	0.9996	0.9985	-0.9964	0.9976	0.9993
A_c/A_f	0.9996	1.0000	0.9989	-0.9956	0.9971	0.9995
A_c/A_m	0.9985	0.9989	1.0000	-0.9942	0.9937	0.9992
A_f/A_z	-0.9964	-0.9956	-0.9942	1.0000	-0.9957	-0.9961
A_c/A_i	0.9976	0.9971	0.9937	-0.9957	1.0000	0.9970
A_c/A_s	0.9993	0.9995	0.9992	-0.9961	0.9970	1.0000

Table 5. Approximate Proportions (Percent) of Acyl Groups with Different Numbers of Carbon Atoms in Some Edible Oils and Lard, Taken from the Literature (Belitz and Grosh, 1985)

no. of carbons	sunflower oil	soybean oil	corn oil	sesame oil	olive oil	lard
C:14						2.5
C:16	6.5	10.0	10.5	8.5	13.0	28.0
C:18	91.5	88.5	88.0	91.0	86.5	67.0
C:20	1.5	1.0	0.5	0.5	0.5	2.5

-CH₂- groups, such as A_c/A_i , provide information on the degree of saturation or unsaturation of the sample, although not so accurate as the above-cited ratios.

This fact can be explained since all of the samples here studied, except the lard sample, have similar proportions of acyl groups of each length (see Table 5). If the samples were constituted by acyl groups with the same numbers of carbon atoms, n , there would be three ester groups for each $3n$ carbon atoms of the acyl groups in each molecule of the triglyceride ester in all samples, regardless of the chain unsaturation; in this case, the ratio between absorbances of bands due to the ester group and either to the -CH₂- group or to the =CH- cis group would provide accurate data reflecting the degree of unsaturation of the sample. This fact is also true for samples constituted by the same proportion of acyl groups with different lengths. In the samples here studied only lard shows remarkable differences in the proportion of the acyl groups with different lengths, for this reason also ratios that relate absorptions of ester groups and either of -CH₂- group or =CH- cis group are useful to show the unsaturation or saturation of the samples. The parameters obtained are also similar for sunflower and corn oils.

Other ratios between absorbances of bands either of -CH₂- or of =CH- cis group and bands of the fingerprint region associated with ester groups and -CH₂- groups, such as A_c/A_s , correlate with a high correlation coefficient with all of the above-mentioned ratios.

Table 6. Coefficients (a and b) and Statistics (Correlation Coefficient, R , and Number of Experimental Data, n) of the Equations Iodine Value = $a + b \times$ Ratio, Which Relate Iodine Values and Ratios of Some Infrared Spectra Bands Absorbances

eq	ratio	a	b	n	R
1	A_c/A_e	4.57	751.70	16	0.9974
2	A_c/A_f	7.12	435.92	16	0.9979
3	A_c/A_i	-51.49	849.04	16	0.9946
4	A_c/A_s	-43.03	320.25	16	0.9965

To prove if all of these parameters are related to the IV, the latter was determined and the values obtained are given in Table 1 together with their standard deviations. It can be observed that the IV of lard is the lowest and is in agreement with the values in the literature (Arnold and Hartung, 1971); the IV of the five samples of olive oil are also similar. Sesame oil and oil of unknown seeds show an intermediate value, and the highest values correspond to sunflower, corn, and soybean oils. However there are two samples of sunflower oil, samples M and O, that are the least saturated of all and for that show the highest IV. Table 6 shows some equations as examples of the close relationships found between some of the above-cited absorbance ratios, given in Table 3, and the IV in Table 1 (eq 1, IV = 4.57 + 751.70 A_c/A_e , $R = 0.9974$; eq 2, IV = 7.12 + 435.92 A_c/A_f , $R = 0.9979$; eq 3, IV = -51.49 + 849.04 A_c/A_i , $R = 0.9946$; and eq 4, IV = -43.03 + 320.25 A_c/A_s , $R = 0.9965$). It can be observed that the IV is very closely related to the ratios A_c/A_e , A_c/A_f , and A_c/A_s and that, in general, with all of the other ratios above-mentioned there also exists a very close relationship.

In conclusion, not only are the three bands cited by other authors (bands c, e, and f) useful to calculate the degree of unsaturation of edible oils and fats but also all of the above-mentioned can be used to define this important characteristic of these types of samples. Recently there has been a trend toward obtaining the values of the traditional parameters that characterize edible oils and fats, including the IV, by means of calibrations, using new techniques, including Fourier transform infrared spectroscopy (Van de Voort et al., 1992, 1995), because these latter are more accurate and faster than the old wet methods. However, the ratios described here can be used, without posterior transformation, to define the unsaturation degree of edible fats and oils poor in trans double bonds. These ratios are obtained directly from the infrared spectrum of the sample, without calibrations, in an automatic way,

Table 7. Coefficients (*a*, *b*, and *c*) and Statistics (Correlation Coefficient, *R*, and Number of Experimental Data, *n*) of the Equations Ratio = *a* + *b* × %M + *c* × %P + *d* × %S, Obtained by Fitting of Absorbance Ratios of Specific Bands and the Proportion of Monounsaturated (%M), Polyunsaturated (%P), and Saturated (%S) Acyl Groups of the Samples

eq	ratio	<i>a</i>	<i>b</i> × 10 ²	<i>c</i> × 10 ²	<i>d</i> × 10 ²	<i>n</i>	<i>R</i>
5	<i>A_f/A_u</i>	1.11		-0.30		8	-0.9940
6	<i>A_f/A_n</i>	5.46	3.74		14.83	8	0.9997
7	<i>A_f/A_u</i>	2.83	2.06		4.04	8	0.9992
8	<i>A_f/A_n</i>	9.23		-3.74	10.85	8	0.9995
9	<i>A_f/A_u</i>	4.90		-2.06	1.85	8	0.9992

making use of the software of the equipment, without any previous manipulation of the sample, in a very short period of time, and without using any reagents. For these reasons, in the future instead using the traditional IV, one of the above-cited ratios between absorbances of specific bands could be used; either *A_c/A_f* or *A_c/A_s* could be appropriate to this end.

In a previous paper relationships between the frequency values of some specific bands of the infrared spectra and composition of edible oils, expressed as a percentage of saturated, mono- and polyunsaturated acyl groups, have been found (Guillén and Cabo, 1997b). Taking into account these previous results, relationships between ratios of absorbances of all bands and percentage of saturated (%S), monounsaturated (%M), and polyunsaturated (%P) acyl groups were studied.

At first, monoparametric equations were tested. No close relationship was found between the ratios above-mentioned and the percentage of saturated acyl groups (%S); the closest relationship was found with the ratio *A_f/A_s* with a correlation coefficient of 0.95. The percentage of monounsaturated acyl groups (%M) is closely related to the ratio *A_s/A_u* with a correlation coefficient of 0.9911. Finally, the percentage of polyunsaturated acyl groups (%P) is also closely related to the ratio *A_f/A_u*. Only the equation obtained in this last case given in Table 7 (eq 5, *A_f/A_u* = 1.11 - 0.30 × 10⁻² × %P, *R* = -0.9940) can be considered to have predictive value. Similar results were obtained using the *A_p/A_o* ratio.

Table 8 shows the predicted percentage of polyunsaturated acyl groups, %P, obtained using eq 5. It can be observed that the predicted percentages are very close to the experimental ones. The predicted %P values for olive oil samples B and E are within the normal values for these oils (Belitz and Grosch, 1985), and the values predicted for the rest of the olive oil samples are very close to the experimental ones given in Table 1, except for sample C. In addition, differences between samples are also predicted. The predicted value for sesame oil (sample G) is 46.8%, which is close to experimental data, 42 and 44.5%, given by other authors (Ahmed et al., 1987; Belitz and Grosch, 1985). For the unknown seed oil (sample H) the predicted %P (51.3%) is between those of the sesame and corn oils, in agreement with the IV. Predicted %P values for sun-

flower (samples M-O) and soybean (sample P) oils are in agreement with data from the literature (Belitz and Grosch, 1985), and those of corn oil (samples I and J), corn and sunflower oil mixture (sample K), and sunflower oil (sample L) are very close to the experimental ones in Table 1. In addition, eq 5 predicts lower %P values for corn oils than for sunflower oils, in agreement with experimental data, and the calculated %P values for sample M and O sunflower oils are higher than the corresponding calculated values for sample L and P sunflower oils, in agreement with experimental IV.

Relationships between each one of the calculated absorbance ratios and two of the three %S, %M, and %P values were also tested. Many biparametric equations with high correlation coefficients were found, but the best involve the *A_f/A_n* and *A_f/A_u* ratios, which are given in Table 7 (eq 6, *A_f/A_n* = 5.46 + 3.74 × 10⁻² × %M + 14.83 × 10⁻² × %S, *R* = 0.9997; eq 7, *A_f/A_u* = 2.83 + 2.06 × 10⁻² × %M + 4.04 × 10⁻² × %S, *R* = 0.9992; eq 8, *A_f/A_n* = 9.23 - 3.74 × 10⁻² × %P + 10.85 × 10⁻² × %S, *R* = 0.9995; and eq 9, *A_f/A_u* = 4.90 - 2.06 × 10⁻² × %P + 1.85 × 10⁻² × %S, *R* = 0.9992). Equations with similar predictive value are also obtained with ratios *A_p/A_o* and *A_m/A_o*.

Table 8 gives the predicted percentage of saturated, %S, monounsaturated, %M, and polyunsaturated, %P, acyl groups in the samples, obtained using the system constituted by eqs 6 and 7, on the one hand, and the system formed by eqs 8 and 9, on the other. It can be observed that %P values predicted by means of eqs 8 and 9 are close to those predicted from eq 5 and also to the experimental ones in Table 1. The percentage of saturated acyl groups calculated from eqs 6 and 7, or from eqs 8 and 9, is practically the same and very close to experimental data for all samples. In general, the highest concordance between the predicted and experimental values has found for the percentage of saturated acyl groups. Finally, the percentage of monounsaturated acyl groups obtained from eqs 6 and 7 is also in agreement with experimental values and with literature data (Ahmed et al., 1987; Belitz and Grosch, 1985).

In conclusion, bands of the fingerprint region of the spectrum such as n, o, p, s, t, or u are also important to characterize edible oils and fats. Ratios between absorbances of some specific bands (*A_c/A_f* or *A_c/A_s*) could be used to define the degree of unsaturation of oils with low trans double bond content. Also, ratios of bands such as *A_f/A_u*, *A_f/A_n*, and *A_p/A_u* are highly dependent on the composition of the sample and can be used to predict the proportion of the saturated, monounsaturated, and polyunsaturated acyl groups in oils and fats in a simple, fast, and accurate way. The study was also carried out using band areas instead of band heights, and the results obtained were in agreement in both cases.

Table 8. Proportions of Polyunsaturated (%P), Saturated (%S), and Monounsaturated (%M) Acyl Groups of the Different Samples Predicted with the Equations in Table 7

eqs used	predicted value	sample															
		A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
5	%P	14.9	12.0	9.9	6.9	10.7	7.7	46.8	51.3	58.8	58.9	60.7	62.3	64.0	60.8	64.4	63.8
8, 9	%P	9.8	15.4	12.2	7.7	10.5	9.6	46.1	48.2	60.4	57.2	60.9	61.6	62.9	58.6	60.4	56.3
6, 7	%S	40.5	11.4	13.2	13.2	10.1	13.6	14.9	11.0	12.6	13.0	11.2	14.4	13.8	12.3	14.9	14.4
8, 9	%S	40.5	11.3	13.1	13.2	10.0	13.5	14.9	11.0	12.5	13.0	11.2	14.3	13.8	12.3	14.9	14.6
6, 7	%M	47.5	73.0	74.2	78.6	79.2	76.4	38.5	40.5	26.7	29.4	27.5	23.5	22.8	28.7	24.2	28.8

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