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Application of multivariate chemometric techniques for simultaneous determination of five parameters of cottonseed oil by single bounce attenuated total reflectance Fourier transform infrared spectroscopy

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ABSTRACT

Single bounce attenuated total reflectance (SB-ATR) Fourier transform infrared (FTIR) spectroscopy in conjunction with chemometrics was used for accurate determination of free fatty acid (FFA), peroxide value (PV), iodine value (IV), conjugated diene (CD) and conjugated triene (CT) of cottonseed oil (CSO) during potato chips frying. Partial least square (PLS), stepwise multiple linear regression (SMLR), principal component regression (PCR) and simple Beer's law (SBL) were applied to develop the calibrations for simultaneous evaluation of five stated parameters of cottonseed oil (CSO) during frying of French frozen potato chips at 170 °C. Good regression coefficients (R^2) were achieved for FFA, PV, IV, CD and CT with value of >0.992 by PLS, SMLR, PCR, and SBL. Root mean square error of prediction (RMSEP) was found to be less than 1.95% for all determinations. Result of the study indicated that SB-ATR FTIR in combination with multivariate chemometrics could be used for accurate and simultaneous determination of different parameters during the frying process without using any toxic organic solvent.

1. Introduction

In frying process, food material is cooked in hot fat and oil, generally at temperature between 150 and 190 °C. It involves heat, mass transfer and complex interactions between the material and frying medium. The frying procedure is widely used in homes, eating places, and food industries to convert the food materials more attractive and delicious. Worldwide demand and consumption of fried food is gradually increasing throughout the world [1,2].

During frying process, hydrolysis and oxidation lead to deterioration of frying oils [3–5]. Therefore, monitoring of free fatty acids, peroxide value, iodine value, conjugated diene and conjugated triene is very important. Formation of oxidation product like hydroperoxides, methylene-intervallic dienes or polyenes is due to the shifting of position of their double bonds. Conjugated diene and conjugated triene are also analytical indicators of oxidation and can be determined by UV absorption at 232 and 270 nm, respectively [6]. Primary oxidation products (peroxides) are converted into secondary oxidation products containing carbonyl groups such as ketones, aldehydes and epoxides [7].

Standard methods for the determination of free fatty acids, peroxide value, iodine value, conjugated diene and conjugated triene of edible or frying oils are based on titrimetric and spectrophotometric methods [8–11]. In addition to sensitivity and reproducibility problem, these methods are very laborious and involve health hazardous chemicals and solvents. Furthermore, these methods are expensive and also associated with environmental pollution.

FTIR spectroscopy in combination with chemometrics has been proved to be fast, easy and environment friendly technique. Furthermore, sample preparation for FTIR analysis is very easy and often no sample preparation is required [12,13]. Multivariate chemometrics are capable to provide the precision, accuracy, and analytical information and save a lot of time.

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Already FTIR spectroscopy with multivariate chemometric analysis has applied for determination of some parameters such as free fatty acid [14], peroxide value [15], iodine value [16], conjugated diene and triene [11], carbonyl value [17,18], total polar compounds [19,20], fatty acid composition [21], fatty acid groups [22] and frying oil ratio [23,24]. To the best of our knowledge, no work has been reported on simultaneous determination of FFA, PV, IV, CD and CT of frying oils using multivariate chemometric analysis.

In the present study, we developed the various multivariate chemometric calibrations using single-bounce attenuated total reflection (SB-ATR) FTIR spectroscopy. The developed calibration models were compared and successfully applied for simultaneous assessment of five important parameters of cottonseed oil during the frying process of potato chips.

2. Experimental work

2.1. Chemicals, reagents and samples

All chemicals and reagents used were of analytical and HPLC grade. Iso-octane and anhydrous sodium sulfate were purchased from Sigma Aldrich (USA) and VWR Prolabo (EC), respectively. Refined cottonseed oil (CSO) was obtained by Helvacizade Food Company (Konya, Turkey).

2.2. Frying procedure

In the frying procedure, French frozen potato chips (SuperFresh, Turkey) were purchased from the local market of Konya, Turkey. The frozen potato chips frying process was carried out for 10 h in a 2 L cottonseed oil at 170 ± 5 °C with thermostatic temperature control in deep fryer named as Arzum AR 260 SPİNFRY FRİTÖZ. When the oil reached at mentioned temperature, 8% of frozen potato chips/oil was placed into the hot oil for each batch cycle and the frying performance was carried out for one more batch cycle in one hour frying period. The frying time was set at 8 min for each batch cycle. Total 20 batch cycles were performed for total 10 h frying period. After every one hour of frying process, the 50 mL of fried oil samples were collected and cooled at a room temperature. Further, the frying oil samples were capped into brown glass-stoppered flasks and stored in refrigerator to protect for deterioration until the analysis. The volume of oil was not refilled during the entire frying period. Total 10 oil samples were collected.

2.3. Method of free fatty acid analysis

FFAs content as % of oleic acid was determined by the titration of a solution of oil dissolved in hot neutral ethanol (C_2H_5OH) with 0.1 N NaOH solutions along with indicator (phenolphthalein in 1% C_2H_5OH) using AOCS standard procedure named as Ca 5a-40 [25].

2.4. Method of peroxide value

PV is expressed as milli-equivalents of oxygen kg^{-1} of oil ($meqO_2$/kg of oil) and determined using AOCS Official Method Cd 8-53 [25]. According to standard procedure, oil was dissolved in chloroform and glacial acetic acid mixture ($CHCl_3$/CH_3COOH 40:60) and allowed to react with freshly prepared potassium iodide (KI) solution in the absence of light. Free iodine (I_2) was determined by titrating the mixture against standard sodium thiosulfate ($Na_2S_2O_3$; 0.01 M)) solution using starch as an indicator.

2.5. Method of iodine value

IV determined unsaturation degree present in fats/oils. The IV is the amount of I_2 (g) absorbed by 100 g of the oil determined by the Wijs method using carbon tetrachloride (CCl_4) as a solvent, according to the IUPAC Official Method 2.205 [26]. FO was mixed in Wijs solution and KI solution (10%). Free I_2 was determined by titrating with standard $Na_2S_2O_3$ solution (0.1 M), using CCl_4 as a blank and starch (1%) as an indicator.

2.6. Method of conjugated diene and triene

The European Communities official method was used for the determination of CD and CT in oil samples [27]. 0.1 g of oil sample was placed in 10 mL of volumetric flask and dissolved with Iso-octane (9.9 mL) to make up the volume, and more diluted by taking 0.1 mL from prepared stock solution and 9.9 mL of Iso-octane for the analysis of CD and CT. Absorbance was measured at 232 and 270 nm by a UV–visible spectrophotometer (Perkin Elmer Lambda 35) with a 1 cm quartz cell.

2.7. Procedure of SB-ATR FTIR calibration standards

Eleven calibration standards were prepared by gravimetrically mixing of fresh and 10 h fried cottonseed oil with different ratios. Standard reported methods were used to measure exact values of FFA, PV, IV, CD and CT of prepared standards. Calibration models were developed for the determination of FFA (%), PV ($meqO_2$/kg of oil), IV (g/100 g), CD (g/L) and CT (g/L) using different chemometric techniques.

2.8. SB-ATR FTIR spectra acquisition

All infrared spectra (IR) of calibration standards and frying oil samples were recorded on a FTIR spectrometer (Perkin Elmer spectrum 100) fitted with deuterated triglycine sulfate (DTGS) detector. The spectrum software version 6.3.5 (Perkin Elmer, Inc.) was used for data acquisition and instrument control. IR spectra were collected in the mid IR region (4000–650 cm^{-1}) at 32 scans and 4 cm^{-1} resolution using a removable ZnSe SB-ATR universal sampling accessory. Approximately 20 µl of oil was poured onto the crystal material for spectra recording. After each standard and sample, the crystal was carefully cleaned with soft tissue than n-C_6H_{14}, followed by acetone (C_3H_6O) wash to remove any possible contamination. Prior to spectra of each standard and sample, fresh background spectrum of air was taken for accurate quantitative analysis.

2.9. Chemometric treatments of SB-ATR FTIR spectra

Multivariate chemometrics such as PLS, SMLR, PCR and SBL were applied on the spectra obtained from SB-ATR FTIR using Turbo Quant (TQ) analyst 7.2 software (Nicolet Madison, WI, USA). Multivariate calibration models for FFA, PV, IV, CD and CT were developed using the reference values (obtained from reported methods) and predicted values in TQ Analyst software. The performance of the models were carried out in terms of root mean square error of calibration (RMSEC), root mean square error of prediction (RMSEP) and root mean square error of validation (RMSECV) as per the protocol of reported methods [28,29].

3. Results and discussion

Basically FTIR confirms either the presence or absence of specific functional groups. As all vegetable oils have common functional groups therefore joint bands are present in the group

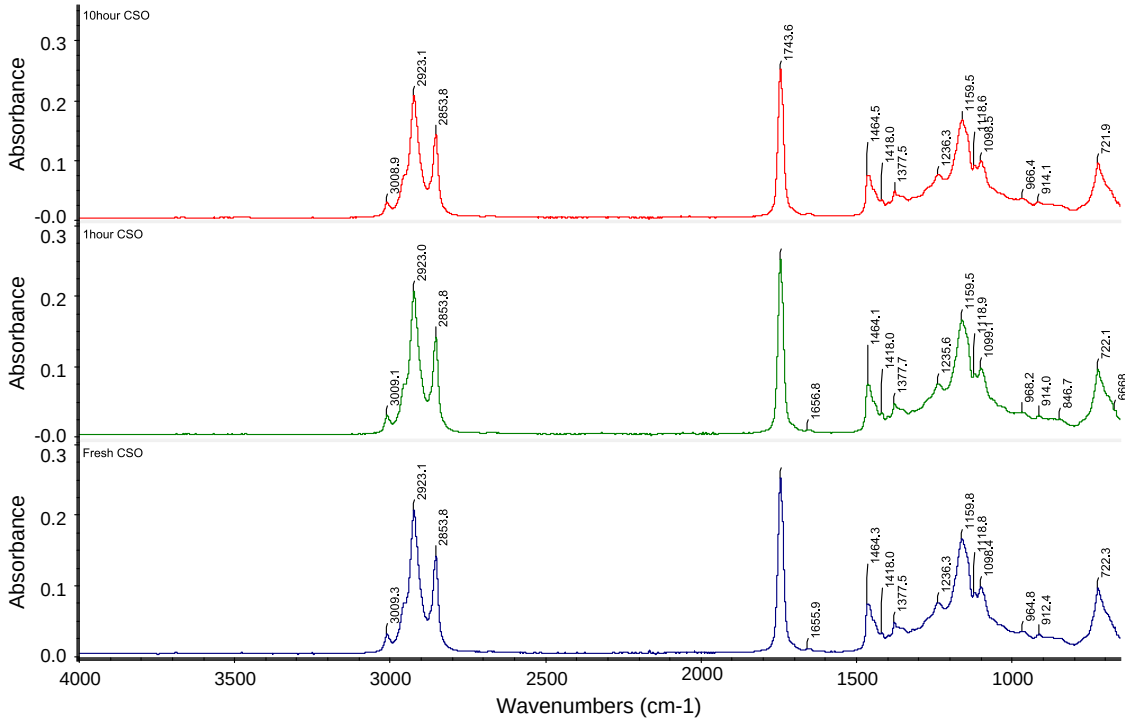

Fig. 1. Representative FTIR spectra of fresh, 1 h and 10 h fried cottonseed oil samples.

spectra of vegetable oils as shown in Fig. 1. Only difference in the height or area was observed. The hydroperoxide shows the peak at 3471 cm^{-1} indicating the presence of free fatty acids [30]. The band of stretching vibration of *cis* double bond of unsaturated fatty acids was observed at 3008 cm^{-1}, where an asymmetrical and symmetrical C–H stretching band shows the absorbance at 2929 and 2856 cm^{-1} fatty acid hydrocarbon chain [31]. The C═O stretching (ester) strong band appears at 1749 cm^{-1}. Aldehydes and ketones show their peaks at 1725 and 1715 cm^{-1}, respectively for their functional groups [18]. The peak at 1652 cm^{-1} indicated the C═C stretching vibration of *cis*-olefins. The bending vibrations of CH_2 andCH_3 aliphatic groups correspond to band at 1460 cm^{-1} [31]. The bands at 1375 and 1236 cm^{-1} are related with the bending vibrations of CH_2 groups. The bands at 1236, 1163, 1116, and 1096 cm^{-1} are due to the stretching vibrations of the C–O ester group, *trans* fat at 968 cm^{-1}.

3.1. Calibration studies for FFA, PV, IV, CD and CT

Fig. 2 shows the FTIR group spectrum of ten calibration standards of the mid IR region (4000–650 cm^{-1}). Group file of the calibration spectra of frying oils from OMNIC program was shifted to TQ Analyst software to get calibration models for FFAs, PV, IV, CD and CT. The reference values of FFA, PV, IV, CD and CT were obtained by reported standard methods.

For the generation of calibration plot for FFA, PV, IV, CD and CT, no any individual region provided satisfactory results in terms of calibration and prediction in PLS, SMLR and PCR and SBL chemometric methods. Consequently different regions were selected by TQ software on the basis of either bands area or bands height. For PLS selected region were 781.03–669.18 cm^{-1}, 1126.22–946.88 cm^{-1}, 1793.47–1508.06 cm^{-1}, 2154.10–1940.04 cm^{-1}, 3045.05–2815.56 cm^{-1}, 3741.23–3598.52 cm^{-1} and 3874.29–3851.15 cm^{-1}. For SMLR, different regions containing 698.10, 700.03, 971.95, 1349.93, 2026.82, 2084.67, 2576.43, 3004.55 and 3100.97 cm^{-1} were picked while for PCR, the selected regions were 944.95–657.61, 1336.43–1016.30, 1793.47–1340.28, 2534.01–1936.18 and 2946.70–2705.64 cm^{-1}. Similarly, for SBL different mid IR regions suggested were 1959.32–1700.00, 3450–2980, 3070–3005, 1186–1178 and 1186.01–1178.29 cm^{-1} as shown in Figs. 3–7. Collectively all selected regions behaved very well for calibration models of FFA, PV, IV, CD and CT as compared to individual region.

3.2. Free fatty acids

Application of PLS, SMLR, PCR and SBL chemometric techniques was carried out on FFAs standards ranged between 0.02 and 0.68%. Reasonable values of R^2, RMSEP, RMSEC and RMSECV were obtained from PLS to be 0.999, 0.030, 0.004 and 0.087, respectively. For SMLR, the values of R^2, RMSEP, RMSEC and percentage of variability were found to be 0.997, 0.138, 0.015 and 99.4%, respectively. The values of R^2, RMSEP and RMSEC for PCR model were determined to be 0.999, 0.071 and 0.004, respectively. While for SBL, the values of R^2 and RMSEP were 0.905 and 0.180, respectively.

3.3. Peroxide value

Calibration models for the determination of PV were used on standards ranged between 0.79 and 4.31 meqO_2/kg of oil. The models were developed by TQ software on different regions, which are already mentioned in Section 3.1. It shows the better results in all calibration models. The performance of the models was checked in the terms of R^2, RMSEP, RMSEC and RMSECV. For PLS model, values were found to be 0.999, 0.340, 0.028 and 0.493. For SMLR values of R^2, RMSEP, RMSEC and percentage of variability were determined to be 0.997, 0.588, 0.087 and 99.5%, respectively. R^2, RMSEP and RMSEC for PCR model were found to be 0.999, 0.585 and 0.027, respectively. While, for SBL values of R^2 and RMSEP were 0.966 and 1.17, respectively.

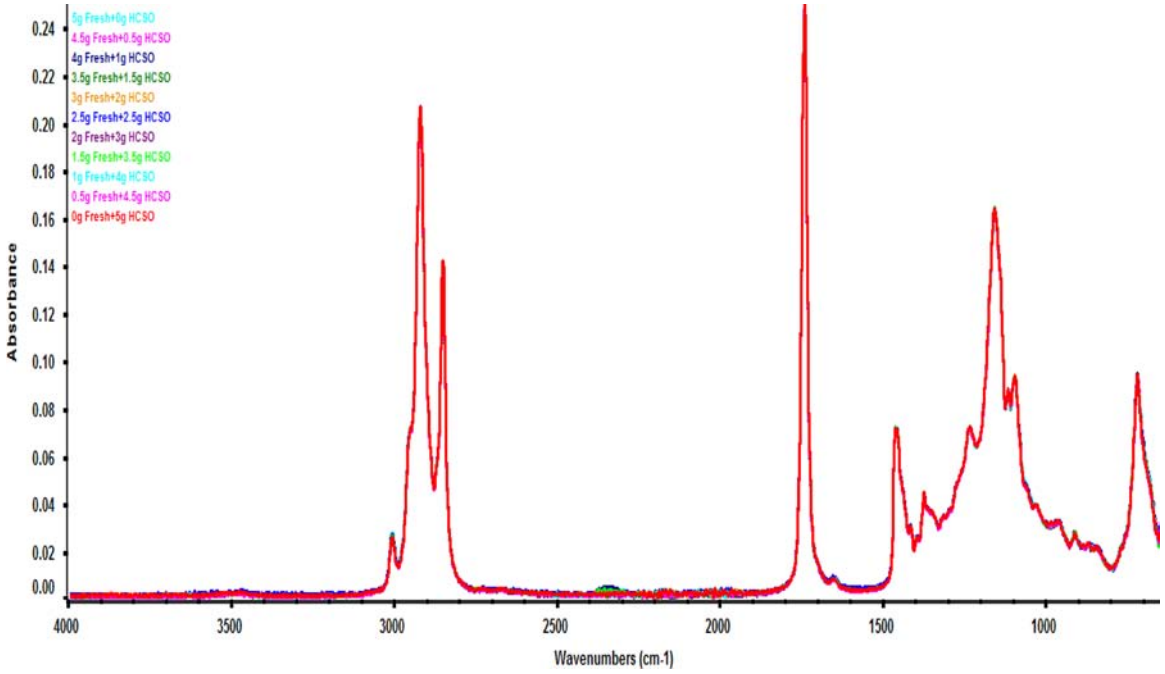

Fig. 2. Group spectra showed the calibration samples for different ratios of fresh and 10 h fried cottonseed oil by SB-ATR-FTIR.

3.4. Iodine value

The calibration models for determination of IV was applied on standards ranged between 109.85 and 115.67 g/100 g. For PLS model, the values of R^2, RMSEP, RMSEC and RMSECV were found to be 0.996, 0.358, 0.133 and 0.827, respectively. The values of R^2, RMSEP, RMSEC and percentage of variability for SMLR model were determined to be 0.997, 1.95, 0.109 and 99.6%, respectively. R^2, RMSEP and RMSEC values for PCR model were found to be 0.999, 0.553 and 0.061, respectively. Similarly, for SBL values of R^2 and RMSEP were 0.986 and 1.67, respectively.

3.5. Conjugated diene

The calibration models of CD were used on standards ranged between 0.60 and 1.53 g L^{-1}. The calibration plot values of R^2, RMSEP, RMSEC and RMSECV for PLS model were 0.997, 0.077, 0.021 and 0.130, respectively. For SMLR model, the values of R^2, RMSEP, RMSEC and percentage of variability were found to be 0.996, 0.139, 0.024 and 99.3%, respectively. The values of R^2, RMSEP and RMSEC for PCR calibration model were found to be 0.996, 0.147 and 0.025, respectively. For SBL model, R^2 and RMSEP values were determined at 0.807 and 0.285, respectively.

3.6. Conjugated triene

The calibration models were developed on the standards ranged between 0.15 and 0.33 g L^{-1} for the determination of conjugated triene in the in frying oils using different chemometric techniques. For PLS model, the values of R^2, RMSEP, RMSEC and RMSECV were determined to be 0.995, 0.005, 0.005 and 0.029, respectively. The values of R^2, RMSEP, RMSEC and percentage of variability for SMLR model were found to be 0.992, 0.057, 0.006 and 98.6%, respectively. R^2, RMSEP and RMSEC values for PCR model were 0.998, 0.010 and 0.002, respectively. For SBL model, the R^2 and RMSEP values were 0.820 and 0.038, respectively.

On the basis of statistical values comparatively PLS provided better results and SBL bears poor results. However, all calibration models are within range of acceptability and could be applied according to expertise of the investigator and facilities.

The statistical results of all calibration models to determine FFAs, PV, IV, CD and CT using SB-ATR-FTIR spectroscopy are shown in Tables 1 and 2. The performance of the methods were performed in terms of regression coefficient (R^2), root mean square error of calibration (RMSEC), root mean square error of cross validation (RMSECV), and root mean square error of prediction (RMSEP). The parameters which were obtained after multivariate calibration models are useful for appraising the analytical worth of the proposed FTIR method. The number of factors, principal components and percentage of variability were used in the calibration models which were automatically selected by the TQ analyst software. For each calibration model, 10 calibration points (o) and 2 validation points (+) were used to check the accuracy. The low values of RMSEC, RMSEP, RMSECV and highest value of R^2 for FFAs, PV, IV, CD and CT demonstrated the goodness and suitability of the method for the proposed chemometric models. FTIR spectral pre-treatment and data correction were carried out as reported earlier [32]. The predictability of the models was tested by computing RMSEP according to reported studies [33,34].

3.7. Method validation

The PLS, SMLR, PCR and SBL calibration models were validated by standard reported methods. Frying cottonseed oil samples which were obtained after each hour frying of French frozen potato chips were analyzed for FFAs, PV, IV, CD and CT by FTIR and through their respective standard methods. From FTIR method it is very easy to determine the values of FFAs, PV, IV, CD and CT by just clicking the button of quantify in TQ software from single spectrum. Tables 3–6 shows the comparable results of reported and proposed methods of frying cottonseed oil samples. The FFA, CD, CT were linearly increased and IV was decreased with increase of frying cycles. But PV increased firstly and after some time it was decreased due to the development of secondary oxidation products. The values of FFA, PV, IV, CD and CT in frying cottonseed oil

Table 1
Statistical results of calibration samples for the determination of FFA, PV, IV, CD and CT by PLS and SMLR chemometric methods using SB-ATR-FTIR spectroscopy***.

Oxidation parameters	Calibration ranges	Spectral regions (cm^{-1})	PLS*					SMLR**			
			Region type	R^2	RMSEC	RMSEP	RMSECV	Region type	R^2	RMSEC	RMSEP
FFA[a] (%)	0.02–0.68	Both method selected different regions	Spectrum range	0.999	0.004	0.030	0.087	Interp height	0.997	0.015	0.138
PV[b] ($meqO_2$/kg of oil)	0.79–4.31	Both method selected different regions	Spectrum range	0.999	0.028	0.034		Interp height	0.997	0.087	0.588
IV[c] (g/100 g)	109.85–115.67	Both method selected different regions	Spectrum range	0.996	0.133	0.358	0.827	Interp height	0.997	0.109	1.95
CD[d] (g/L)	0.60–1.53	Both method selected different regions	Spectrum range	0.997	0.021	0.077	0.130	Interp height	0.996	0.024	0.139
CT[e] (g/L)	0.15–0.33	Both method selected different regions	Spectrum range	0.995	0.005	0.005	0.026	Interp height	0.992	0.006	0.057

[a] Free fatty acids.
[b] Peroxide value.
[c] Iodine value.
[d] Conjugated diene
[e] Conjugated triene.
* Partial least squares.
** Simple multiple linear regression.
*** Single bounce-attenuated total reflectance-Fourier transform infrared.

Table 2
Statistical results of calibration samples for the determination of FFA, PV, IV, CD and CT by PCR and SBL chemometric methods using SB-ATR-FTIR spectroscopy***.

Oxidation parameters	Calibration ranges	Spectral region (cm^{-1})	PCR*				SBL**			
			Region type	R^2	RMSEC	RMSEP	Region type	Spectral region (cm^{-1})	R^2	RMSEP
FFA[a] (%)	0.02–0.68	Selected different regions	Spectrum range	0.999	0.004	0.071	Area	1959.32–1700	0.905	0.180
PV[b] ($meqO_2$/kg of oil)	0.79–4.31	Selected different regions	Spectrum range	0.999	0.027	0.585	Area	3450–2980	0.966	1.17
IV[c] (g/100 g)	109.85–115.67	Selected different regions	Spectrum range	0.999	0.061	0.553	Area	3070–3005	0.986	1.67
CD[d] (g/L)	0.60–1.53	Selected different regions	Spectrum range	0.996	0.025	0.147	Area	1186–1178	0.807	0.285
CT[e] (g/L)	0.15–0.33	Selected different regions	Spectrum range	0.998	0.002	0.010	Area	1186.01–1178.29	0.820	0.038

[a] Free fatty acids.
[b] Peroxide value.
[c] Iodine value.
[d] Conjugated diene.
[e] Conjugated triene.
* Principal component regression.
** Simple Beer's law.
*** Single bounce-attenuated total reflectance-Fourier transform infrared.

Table 3
Prediction the mean values of FFA, PV, IV, CD and CT in frying cottonseed oil samples by reported and SB-ATR-FTIR–PLS methods.

FO samples (Hour)	FFA (%)			PV ($meqO_2$/kg of oil)			IV (g/100 g)			CD (g/L)			CT (g/L)		
	RM[a]	FTIR–PLS[b]	RE[c] (%)	RM[a]	FTIR–PLS[b]	RE[c] (%)	RM[a]	FTIR–PLS[b]	RE[c] (%)	RM[a]	FTIR–PLS[b]	RE[c] (%)	RM[a]	FTIR–PLS[b]	RE[c] (%)
0	0.04	0.05	−25.00	0.79	0.83	−5.06	113.78	113.77	0.008	0.64	0.65	−1.56	0.20	0.20	0.00
1	0.07	0.07	0.00	0.96	0.93	3.12	113.74	113.74	0.00	0.75	0.75	0.00	0.21	0.21	0.00
2	0.11	0.11	0.00	1.28	1.28	0.00	133.77	113.77	0.00	0.81	0.81	0.00	0.21	0.19	9.52
3	0.14	0.14	0.00	1.43	1.43	0.00	112.96	112.96	0.00	0.86	0.86	0.00	0.24	0.25	−4.16
4	0.19	0.18	5.26	1.89	1.86	1.58	112.42	112.43	0.00	0.93	0.92	1.07	0.26	0.29	−11.53
5	0.22	0.22	0.00	2.34	2.33	0.42	112.07	112.08	−0.008	1.00	0.99	1.00	0.25	0.30	−20.00
6	0.25	0.25	0.00	2.69	2.33	13.38	111.98	112.19	−0.18	1.09	1.01	7.33	0.26	0.26	0.00
7	0.29	0.30	−3.44	3.09	3.13	−1.29	111.08	111.08	0.00	1.15	1.16	−0.86	0.32	0.32	0.00
8	0.32	0.32	0.00	3.44	3.44	0.00	110.44	110.44	0.00	1.25	1.25	0.00	0.29	0.27	6.89
9	0.35	0.35	0.00	3.68	3.41	7.33	110.56	110.59	−0.02	1.32	1.27	3.78	0.29	0.25	13.79
10	0.38	0.38	0.00	3.95	3.94	0.25	109.93	109.93	0.00	1.43	1.43	0.00	0.31	0.32	−3.22

[a] Reported method.
[b] Fourier transform infrared–partial least square.
[c] Relative error (actual values − measured values × 100/actual value).

samples from 0 to 10 h were found in the range of 0.04–0.38%, 0.79–3.94 $meqO_2$/kg of oil, 113.78–109.93 g/100 g, 0.64–1.43 g/L and 0.20–0.31 g/L, respectively.

The correlations between FFA vs PV, CD and CT were also observed and shown in Fig. 3a, b and c. PV, CD and CT showed the good relationship with the FFA of frying oils.

Table 4
Calculation the mean values of FFA, PV, IV, CD and CT in frying cottonseed oil samples by reported and SB-ATR-FTIR–SMLR methods.

FO samples (Hour)	FFA (%)			PV (meqO$_2$/kg of oil)			IV (g/100 g)			CD (g/L)			CT (g/L)		
	[a]RM	[b]FTIR–SMLR	[c]RE (%)	[a]RM	[b]FTIR–SMLR	[c]RE (%)	[a]RM	[b]FTIR–SMLR	[c]RE (%)	[a]RM	[b]FTIR–SMLR	[c]RE (%)	[a]RM	[b]FTIR–SMLR	[c]RE (%)
0	0.04	0.06	−50.00	0.79	0.77	2.53	113.78	113.75	0.03	0.64	0.64	0.00	0.20	0.20	0.00
1	0.07	0.08	−14.28	0.96	1.03	−7.29	113.74	113.74	0.00	0.75	0.77	−2.66	0.21	0.20	4.76
2	0.11	0.10	9.09	1.28	1.29	−0.78	133.77	113.77	0.00	0.81	0.78	3.70	0.21	0.23	−9.52
3	0.14	0.12	14.28	1.43	1.36	4.89	112.96	112.95	0.008	0.86	0.84	2.32	0.24	0.19	20.83
4	0.19	0.24	−26.31	1.89	1.84	2.64	112.42	112.33	0.08	0.93	0.91	2.16	0.26	0.26	0.00
5	0.22	0.27	−22.72	2.34	2.33	0.42	112.07	111.96	0.09	1.00	0.98	2.00	0.25	0.25	0.00
6	0.25	0.25	0.00	2.69	2.69	0.00	111.98	111.95	0.03	1.09	1.18	−8.25	0.26	0.25	3.84
7	0.29	0.29	0.00	3.09	3.06	0.97	111.08	111.08	0.00	1.15	1.15	0.00	0.32	0.29	9.37
8	0.32	0.33	−3.12	3.44	3.44	0.00	110.44	110.45	0.009	1.25	1.21	3.20	0.29	0.29	0.00
9	0.35	0.33	5.71	3.68	3.59	2.44	110.56	110.53	0.027	1.32	1.32	0.00	0.29	0.32	−10.34
10	0.38	0.36	5.26	3.95	3.94	0.25	109.93	109.93	0.00	1.43	1.39	2.79	0.31	0.28	9.67

[a] Reported method.
[b] Fourier transform infrared–stepwise multiple linear regression.
[c] Relative error (actual values – measured values × 100/actual value).

Table 5
The mean values of FFA, PV, IV, CD and CT in frying cottonseed oil samples by reported and SB-ATR-FTIR–PCR methods.

FO samples (Hour)	FFA (%)			PV (meqO$_2$/kg of oil)			IV (g/100 g)			CD (g/L)			CT (g/L)		
	[a]RM	[b]FTIR–PCR	[c]RE (%)	[a]RM	[b]FTIR–PCR	[c]RE (%)	[a]RM	[b]FTIR–PCR	[c]RE (%)	[a]RM	[b]FTIR–PCR	[c]RE (%)	[a]RM	[b]FTIR–PCR	[c]RE (%)
0	0.04	0.03	14.28	0.79	0.80	−1.26	113.78	113.53	0.22	0.64	0.59	7.81	0.20	0.22	0.00
1	0.07	0.08	−14.28	0.96	0.92	4.16	113.74	113.46	0.24	0.75	0.68	9.33	0.21	0.18	14.28
2	0.11	0.09	18.18	1.28	1.22	4.68	133.77	113.71	0.04	0.81	0.73	9.87	0.21	0.20	4.16
3	0.14	0.11	21.42	1.43	1.31	8.39	112.96	112.90	0.05	0.86	0.81	5.81	0.24	0.22	8.33
4	0.19	0.18	5.26	1.89	1.85	2.11	112.42	112.40	0.02	0.93	0.91	2.15	0.26	0.27	−3.84
5	0.22	0.20	9.09	2.34	2.30	1.70	112.07	112.02	0.04	1.00	1.03	−3.00	0.25	0.26	−4.00
6	0.25	0.23	8.00	2.69	2.74	−1.85	111.98	111.96	0.02	1.09	1.14	−4.58	0.26	0.25	3.84
7	0.29	0.30	−3.44	3.09	3.14	−1.61	111.08	111.16	−0.07	1.15	1.07	6.95	0.32	0.32	0.00
8	0.32	0.32	0.00	3.44	3.37	2.03	110.44	110.68	−0.22	1.25	1.20	4.00	0.29	0.26	6.89
9	0.35	0.35	0.00	3.68	3.68	0.00	110.56	110.44	0.10	1.32	1.32	0.00	0.29	0.29	0.00
10	0.38	0.35	7.89	3.95	3.91	1.01	109.93	109.93	0.00	1.43	1.43	0.00	0.31	0.29	6.45

[a] Reported method.
[b] Fourier transform infrared–principal components regression.
[c] Relative error (actual values – measured values × 100/actual value).

Table 6
The mean values of FFA, PV, IV, CD and CT in frying cottonseed oil samples by reported and SB-ATR-FTIR–SBL methods.

FO samples (Hour)	FFA (%)			PV (meqO$_2$/kg of oil)			IV (g/100 g)			CD (g/L)			CT (g/L)		
	[a]RM	[b]FTIR–SBL	[c]RE (%)	[a]RM	[b]FTIR–SBL	[c]RE (%)	[a]RM	[b]FTIR–SBL	[c]RE (%)	[a]RM	[b]FTIR–PLS	[c]RE (%)	[a]RM	[b]FTIR–PLS	[c]RE (%)
0	0.04	0.07	−75.0	0.79	0.73	7.59	113.78	113.34	0.38	0.64	0.47	26.56	0.20	0.19	5.00
1	0.07	0.10	−42.86	0.96	0.88	8.33	113.74	113.41	0.29	0.75	0.79	−5.33	0.21	0.20	4.76
2	0.11	0.06	45.45	1.28	1.19	7.03	113.77	113.44	0.29	0.81	0.64	20.98	0.21	0.17	19.04
3	0.14	0.08	42.85	1.43	1.33	6.99	112.96	112.32	0.56	0.86	0.94	−9.30	0.24	0.29	−20.83
4	0.19	0.15	21.05	1.89	1.63	13.75	112.42	112.63	−0.18	0.93	0.83	10.75	0.26	0.34	−30.76
5	0.22	0.16	27.27	2.34	2.16	7.69	112.07	111.91	0.14	1.00	0.91	9.00	0.25	0.18	28.00
6	0.25	0.18	28.0	2.69	2.58	4.08	111.98	111.72	0.23	1.09	1.34	−22.93	0.26	0.14	46.15
7	0.29	0.22	24.14	3.09	2.94	4.85	111.08	110.87	0.18	1.15	0.95	17.39	0.32	0.41	−28.12
8	0.32	0.31	3.12	3.44	3.31	3.77	110.44	110.94	−0.45	1.25	1.25	0.00	0.29	0.15	48.27
9	0.35	0.29	17.14	3.68	3.53	4.07	110.56	110.81	−0.22	1.32	1.17	11.36	0.29	0.26	10.34
10	0.38	0.43	−13.16	3.95	4.06	−2.78	109.93	109.29	0.58	1.43	1.23	13.98	0.31	0.31	0.00

[a] Reported method.
[b] Fourier transform infrared–simple Beer's law.
[c] Relative error (actual values – measured values × 100/actual value).

From the above results obtained here, it was observed that all multivariate chemometric techniques (PLS, SMLR, PCR and SBL) can be used for simultaneous determination of important parameters in fresh and used frying cottonseed oils. Some researchers reported their work on simultaneously determination of two or three parameters. For example, Yu et al. reported the automated, high-speed analysis of edible oils for FFA and PV using a FTIR spectrometer coupled to an auto-sampler [35]. Pintoet al. determined *cis–trans* ratio, hydroperoxides and secondary oxidation products including carbonyl groups in sunflower, olive and canola oils by MIR-ATR-FTIR [36]. Moros et al. determined the unsaturated as well as *trans* fatty acids and free fatty acids by ATR-FTIR spectroscopy in combination with multivariate chemometric techniques [30]. Study of Maylet Hernandez-Martinez et al. revealed that the MID-FTIR spectroscopy with multivariate calibration (PLS-1) was used for the evaluation of various parameters

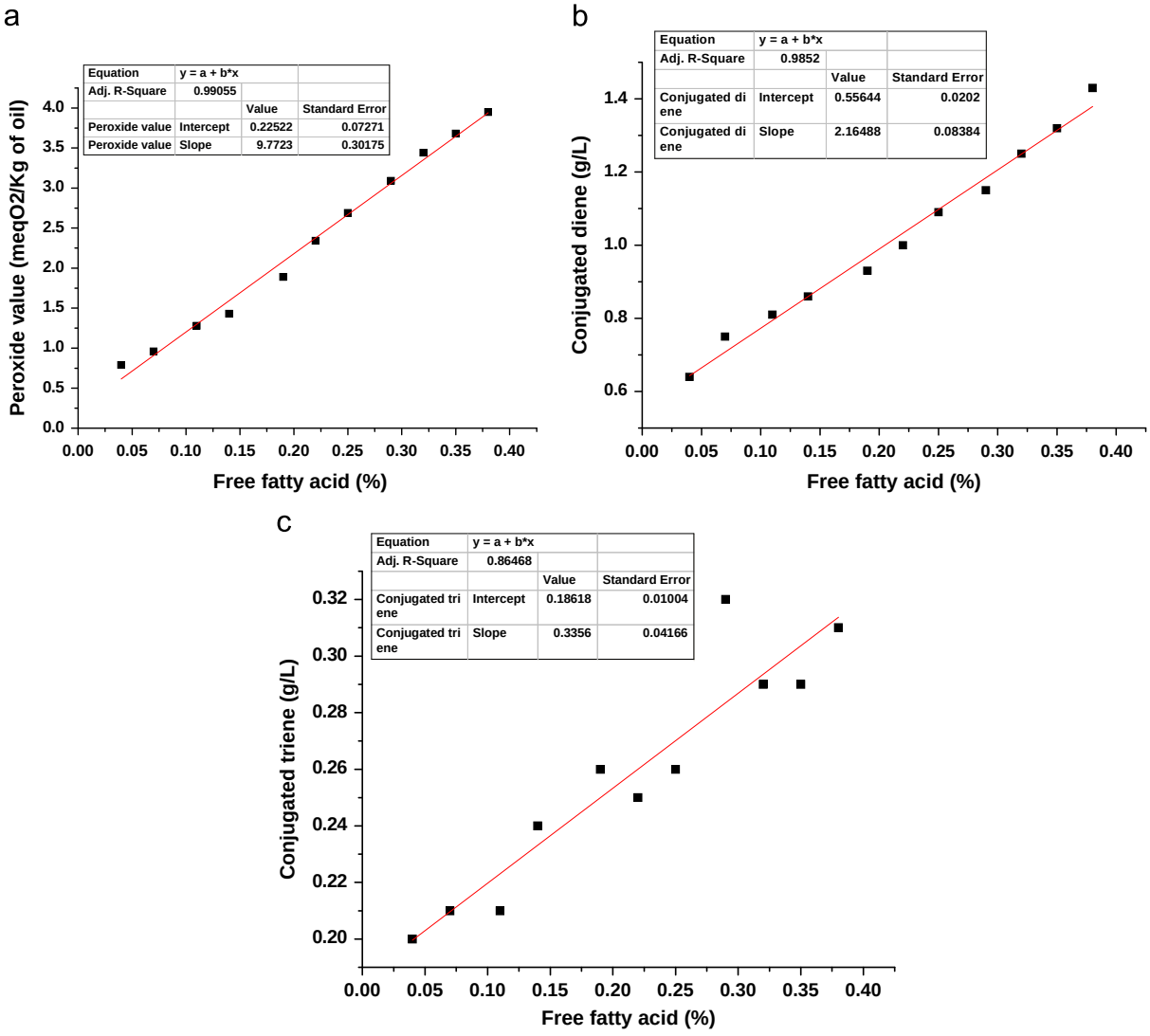

Fig. 3. Correlations of FFA vs PV (a), FFA vs CD (b) and FFA vs CT (c).

such as fatty acid composition and some nutritional parameters of chilled fillets, crevalle jack or Atlantic Spanish mackerel [37]. From the literature, we could not find any study related to simultaneous monitoring of FFA, PV, IV, CD and CT in cottonseed oil.

4. Conclusions

The results of the present study showed that SB-ATR FTIR spectroscopy and multivariate chemometric techniques such as PLS, SMLR, PCR and SBL could be applied for the fast and simultaneous determination of FFA, PV, IV, CD and CT in frying cottonseed oil. Comparatively, PLS has given the excellent results. The merits of developed FTIR method in conjunction with multivariate chemometric models include:

(1) The use of toxic organic solvents/reagents was totally avoided.
(2) Less amount of samples is required for analysis ($< 20\ \mu l$).
(3) Through single spectrum five parameters could be easily determined simultaneously less than 5 min.

The SB-ATR FTIR method is very simple, rapid, environmental friendly and no sample preparation is required for the analysis. For each standard method, 30 min to 2 h are required for the individual determination of FFA, PV, IV, CD and CT.

Results of the study clearly revealed that SB-ATR FTIR in combination with chemometric techniques such as PLS, SMLR, PCR and SBL could be used in the industry as well as analytical laboratories for simultaneous determination of FFA, PV, IV, CD and CT for all vegetable oils using same type of protocols.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.04.002.

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