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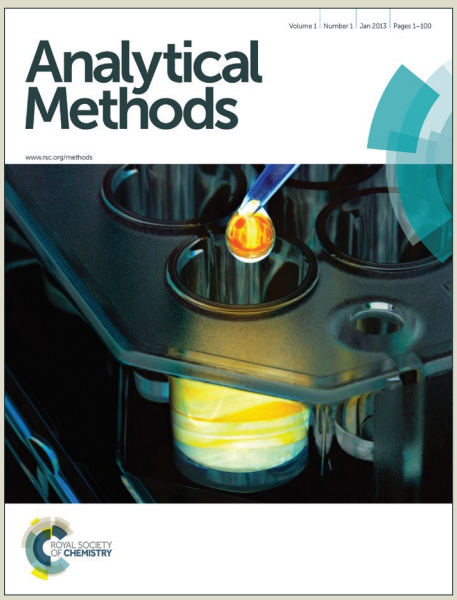

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Assessing Potato Chip Oil Quality using a Portable Infrared Spectrometer Combined with Pattern Recognition Analysis

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ABSTRACT

The objective of this study was to evaluate the performance of a portable FT-IR spectrometer equipped with a 5-bounce heated ZnSe crystal to develop classification methods for authentication of potato chip frying oils and to generate prediction models for monitoring oil quality parameters for real-time and field-based applications. Oil from commercial potato chips (n=95) were expelled mechanically by a hydraulic press and their fatty acid profile determined by GC-FAME to identify the oil type used for chip manufacturing. Peroxide value (PV), free fatty acids (FFA), and *p*-anisidine value (*p*-AV) were also evaluated to determine quality parameters of the oils. IR spectra were collected using a portable FT-IR equipped with a heating stage (65°C) and analyzed by pattern recognition using Soft independent modeling of class analogy algorithm (SIMCA) and partial least squares regression (PLSR). SIMCA showed that different oil types successfully formed distinct clusters allowing detecting mislabeling of frying oils in commercial chips. PLSR models predicted fatty acid profile (GC-FAME) with excellent correlation ($R_{cal} \geq 0.93$) and standard error of cross-validation (SECV) of ~1.0% for major fatty acids. Models for FFA, PV and *p*-AV gave $R_{cal} \geq 0.93$ and SECV of 0.05%, 1.27 meq/kg, and 5.94 p-AV, respectively. Profits and trading advantages from mislabeling prejudice consumers and manufacturers, and our data supports that IR portable instruments present great potential for *in-situ* surveillance of vegetable oils used for potato chip frying.

Key words: Potato chips, oil, infrared spectroscopy, chemometrics, quality

1. INTRODUCTION

Potato chips has been a popular snack since its accidental birth in 1853 and reported $5.7 billion sales annually in the US market, which represents 20% of total US snack market [1,2]. Lipids are a major component in potato chips representing between 35 to 44% of the product composition [3]. Vegetable oils serve as frying medium to promote heat transfer and give the desired texture and flavor [4] to the potato chips. Different types of vegetable, partially hydrogenated or blends of oils are used for deep fat frying [6]. Important characteristics in selecting frying oils are high oxidative stability, high smoke point, low foaming, low melting point, bland flavor, availability, nutritional value, and cost [5]. Most common frying oils in the potato chips industry come from corn, canola, sunflower (mid-oleic and high-oleic variants), high oleic (HO) safflower and cottonseed oils [6]. Although partially hydrogenated oil improves resistance to rancidity it is phasing out because of trans fat health concerns by consumers [7]. Preference of blended vegetable oils over a sole type is because of the economic purposes, improved resistance to oxidation and longer shelf life [8]. In addition, over the past years various oils have been developed with modified fatty acid composition through plant breeding improving their oxidative stability by accumulating oleic acid (>80%) and reducing the levels of polyunsaturated fatty acids (3-10%); some examples include low-linolenic soybean, HO sunflower, low-linolenic canola, HO canola, and HO corn oils [9,10].

Edible oils and fats are one of the most counterfeited foods in the industry [11]. Canola, soybean, and palm oil are the cheapest oils in the market, and used as adulterants in the market [12].To evaluate the quality parameters and authenticate oils and fats, the American Oil Chemists' Society (AOCS), Association of Official Analytical Chemistry (AOAC), the International Union of Pure and Applied Chemistry (IUPAC), and the Federation of Oil Seeds and Fats Association

(FOSFA) have proposed different methods such as determination of fatty acid composition, *trans* fatty acids, sterol composition and content or aliphatic alcohols by chromatography; determination of free fatty acids and peroxide value by titrimetric methods; or using stable isotope ratio analysis [12,13]. However, these traditional methods are time consuming, costly, use toxic reagent, generate large amount of waste, and to obtain accurate results the analyst has to follow rigid rules [14].

To discourage food fraud, analytical methods should be rapid, simple, reliable, cost effective, and need minimum sample preparation [14]. Vibrational spectroscopy and chemometrics provide an alternative to traditional techniques to characterize and authenticate oils and fats [14,15] and to quantitate specific quality parameters including peroxide value, free fatty acids, *trans* fat contents, iodine values, saponification number of edible oils [16,17]. **Table 1** summarizes the performance characteristics of Fourier transform infrared (FT-IR) and near infrared (NIR) spectroscopy for assessing lipid quality. Although, NIR spectroscopy has been reported for classification of oil and fat products [18], its broader and weaker bands provide less spectral details than FT-IR that gives fingerprinting capabilities enabling unique structural identification [18,19]. FT-IR with ATR or transmission cell accessories have been used to classify [18] and authenticate [20] oils. Portable/handheld optical systems for chemical identification has incorporated the analytical precision of spectroscopy to field applications with spectral resolution equivalent to bench-top instruments. These portable devices have been successfully applied for predicting oil quality parameters including monitoring total *trans*-fats [21], authentication [22], oil oxidative stability [23], and free fatty acids in edible oils [24]. Field-deployable fingerprinting approaches for authentication and untargeted detection of economic adulteration can help to streamline quality

assurance detecting tainted ingredient before they have been diluted or combined with other ingredients.

The objective of this study was to evaluate the performance of a portable FT-IR spectrometer equipped with a 5-bounce heated ZnSe crystal to develop reliable classification methods for authentication of potato chip frying oils and to generate prediction models for monitoring oil quality parameters for real-time and field-based applications.

2. MATERIALS AND METHODS

A total of 95 potato chips samples were purchased from local grocery stores in Columbus, OH and the oil extracted using hydraulic press (3851 Benchtop Laboratory Manual Press, Carver, Inc. Wabash, IN). The stainless steel cylindrical container was filled with crushed potato chips, placed under the press and pressure was applied until reaching 15,000 psi. The oil was collected in a stainless steel plate, transferred to dark glass vials and stored at -18°C until further analysis. In addition, 9 different vegetable oils (corn, canola, cottonseed, peanut, sunflower, expeller-pressed sunflower, high oleic (HO) canola, HO sunflower, HO safflower) were kindly provided by a snack food manufacturer.

2.1. Reference Methods

Determination of fatty acid profile was done using a fatty acid methyl ester (FAME) procedure [25] with modifications. Methyl ester forms were generated by dissolving 100 µl oil sample with 10 ml of hexane into a glass tube, 100 µl 2N potassium hydroxide in methanol was added to the tube and vortexed for 30 sec. 1.5 ml aliquot was placed in a micro centrifuge tube and rotated at 13.2 rpm for 5 minutes. The supernatant was transferred into a 2 ml glass vial and used for further analysis. Methyl esters' analyses were carried out in duplicate by using an Agilent 6890

series (Santa Clara, CA) gas chromatography (GC) equipped with a flame ionization detector (FID) and a HP G1513A auto sampler and a tray. Fatty acids' separation was achieved by using HP-88 60m x 0.25mm x 0.2µm column (Agilent 112-8867) by using helium, which was carrier gas. The injection volume was 1 µL with a split ratio of 20:1. The oven conditions were 110˚C for 1 min, to 220˚C (5°C/min) hold for 15 min. The injector temperature was 220˚C and the detector temperature was 250˚C. Fatty acids were identified by comparing the retention times of each peak against reference standards (Supelco® 37 Component FAME Mix, Sigma Aldrich, St. Louis, MO, USA). GC-FAME analysis was done in duplicate. Saturated and polyunsaturated (PUFA) fatty acids were calculated by adding palmitic and stearic acids, linoleic and linolenic acids, respectively.

2.2. Monitoring Oxidative Stability

AOCS official method Cd8-53 [26] was used to determine the peroxide value (PV) using a Metrohm, 916 Ti-Touch (Herisau, Switzerland) automatic titrator. Free fatty acid (FFA) value was determined by using the AOCS official method Ca 5a-40 [27] with European Pharmacopoeia 5.0 01/2005:20501 [28] modifications. The FFA analysis was performed using an automatic titrator (Easy Plus Titration, Mettler Toledo, Greifensee, Switzerland). The *p*-anisidine value (*p*-AV) was determined using AOCS Official Method Cd 18-90 [29] using a Varian spectrophotometer (Agilent, Cary 50 Bio UV/Visible, Santa Clara, CA) to determine absorbance at 350 nm. Oxidative stability tests were done in duplicate.

2.3. FT-IR Spectroscopy

The samples were tempered to 65˚C prior to the measurements using a lab oven (Precision Standard Incubator, PR205125G, Thermo Fisher Scientific, Waltham, MA, USA). All spectral

measurements of oils were done in duplicate. Spectra was collected with a portable (Cary 630, Agilent Technologies Inc., Santa Clara, CA, USA) spectrometer equipped with a temperature controlled, 5-bounce ZnSe crystal attenuated total reflectance (ATR) set to 65°C to prevent fat solidification and 75µl oil aliquot was deposited onto the crystal as shown in **Figure 1a**. Oil spectrum was collected over a range from 4000-700 cm^{-1} at 4 cm^{-1} resolution, and an interferogram of 64 scans was co-added, to produce a final signal averaged spectrum with an improved signal to noise ratio [30]. Spectral data was displayed in terms of absorbance and viewed using Resolutions Pro Software (Varian, Palo Alto, CA, USA).

2.4. Data Analysis

The spectra were analyzed using multivariate statistical analysis software (Pirouette® version 4.0, Infometrix Inc., Woodville, WA, USA). FT-IR spectra were divide by (sample 2-norm) and second derivative (second order poly-nominal filter with a 35 point window) transformed to resolve peak overlap and eliminate baseline shifts [31]. Probability threshold was set as 0.95 for all prediction models.

Fatty acid composition, PV, FFA, *p*-AV reference values were correlated with the infrared spectra using partial least squares regression (PLSR) model. PLSR models were evaluated using leave-one-out cross validation. Integrity of fit was evaluated using correlation coefficient (R^2), standard error cross-validation (SECV), residual analysis, outlier diagnostics, leverage, and standard error of prediction (SEP). The number of PLSR factors that gave the minimum SECV value was considered to be the optimal factor for each model. Residual predictive deviation (RPD), the ratio between the standard deviation (SD) of the reference data to the SEP, was used to assess the model prediction performance. The higher the RPD, the more accurate the data

predicted by the calibration model, with RPD 2.5 to 4.9 considered satisfactory for screening, 5.0 to 6.4 categorized as a good prediction for quality control applications, while above 6.5 are considered as an excellent prediction for process control applications [32]. To predict fatty acid composition, PV, FFA, *p*-AV, that data set was divided into a calibration and validation set. Validation set included the 20% of the total sample size for each test.

As illustrated in **Figure 1b**, when an unknown sample of potato chip oil belonging to the independent validation set was deposited onto the crystal and the spectra was collected, all the quality parameters that studied in this study were predicted simultaneously using the calibration models loaded into the FT-IR spectrometer.

Soft independent modeling of class analogy algorithm (SIMCA), a classification procedure based on the principal component analysis (PCA), was used to cluster oil samples based on their vegetable sources. SIMCA's discriminating power plot was used to identify important infrared bands associated with the sample classifications. If the interclass distances were above 3, classes were considered as significantly different [33] from each other. Independent external validation set used to evaluate the predictive accuracy of the model, 80% of the samples used to generate the calibration models and 20% serve as an independent validation set.

3. RESULTS AND DISCUSSION

3.1. Vegetable Oil Classification

Figure 2 a and **b** shows the overlapped MIR spectra and second derivative spectra of three different potato chip oils (corn, cottonseed and high oleic (HO) canola (II)) indicating the close similarity in spectral characteristics of the vegetable oils. The most prominent absorption regions were found in the 3010-2800 cm^{-1} range associated with =C–H *cis* stretching, -C–H symmetric

and asymmetric stretching vibrations (CH_2 and CH_3), the band centered at 1746 cm^{-1} related to –C=O ester stretching vibration [19], the bands at 1465 and 1377 cm^{-1} that corresponded to C-H bending (symmetrical and scissoring) vibrations of CH_2 and CH_3 groups and the fingerprint region from 1200-1000 cm^{-1} associated with stretching and bending vibrations of –C–O and –CH_2– vibration modes [19,34]. Although the oil spectral patterns were very similar, differences in triglyceride fatty acid composition (chain length, PUFA/saturated ratio, substitution patterns) resulted in slight changes in band intensities and shift in maximum absorbance frequencies for functional groups [19,22]. Intensity of the olefinic band at 3010 cm^{-1} indicated polyunsaturation degree of the oils [19], with corn and cottonseed oils showing increased band intensity than HO canola oil because of their higher content of polyunsaturated (linoleic and linolenic) fatty acids. Corn, cottonseed and HO canola oils contained 58, 57, and 20% polyunsaturated fatty acids, respectively (**Table 2**). Another spectral difference among oils was observed at 1118 cm^{-1}, associated with the stretching vibration of ether linkage in triacylglycerols [19], and was inversely related to the content of saturated acyl groups with HO canola (6%) having the most intense band followed by corn (14%) and cottonseed (26%) oil that had the lowest band height (**Figure 2**).

To develop a calibration model for identification of the type of oil used for manufacturing of potato chips, we first profiled all the oils by GC-FAME to detect the use of one or more vegetable oils in the samples (**Table 2**). Overall, oleic and linoleic acids were the predominant fatty acids with levels ranging from 15 to 86 (55±19%) and 7 to 65% (32±16%), respectively. Out of 95 potato chip samples, we found 69 that contained a sole source of vegetable oils. HO sunflower (80±3%), HO safflower (76±1%) and HO canola (74±2%) showed the highest level of oleic acid, while the rest ranged from 17 to 68%. Corn (57±1%) and cottonseed (57±2%) showed the highest linoleic acid content. The fatty acid levels reported for the different vegetable oils

were in agreement with those reported in the literature [35,36]. In the case of canola oils, we found three different fatty acid profiles associated with regular canola and HO canola oils. The canola oil extracted from potato chips had slightly higher oleic acid (65±1%) levels when compared levels reported in literature (~60%) [37]. Interestingly, we obtained two different profiles for HO canola oils used in manufacturing potato chips with the main difference associated to their oleic and linoleic acids contents (**Table 2**); HO canola (I) had lower oleic (68±0%) but higher linoleic (23±0%) acid content than the HO canola (II) that showed levels of oleic and linoleic of 74±2% and 17±2%, respectively. Genetic mutation have segregated plant cultivars that accumulate significantly more oleic acid (>70%) than the traditional varieties resulting in HO soybean oil, HO sunflower oil, HO safflower, HO peanut oil and HO rapeseed (canola) cultivars [38,39]. HO canola varieties with similar oil composition profiles to those found for HO canola (I) and (II) have been reported by Xu, Tran, Palmer, White, & Salisbury (1999) [40] and Matthäus (2006) [38], respectively. Similarly, we found 2 groups of sunflower oils, a mid-oleic sunflower oil containing 65±1% oleic and 26±2% linoleic and a HO sunflower with 80±3% oleic and 12±2% linoleic acid, in agreement to findings by Tarrago-Trani, Phillips, Lemar, & Holden (2006) [41].

Soft Independent Modeling of Class Analogy (SIMCA) analysis of FT-IR spectra collected from the different frying potato chip oils showed distinctive clustering patterns and 10 well-defined groups for different sole source oils (**Figure 3**) based on GC-FAME profile. SIMCA's projection plot using the first 3 principal components enabled to visualize the natural clustering of samples, and the greater the cluster distances the greater the differences in their chemical composition. The interclass distances (ICD) are Euclidian distances between centers of clusters and are good indicators of class separation in a SIMCA model with ICD ≥3 are considered significant for identification [33]. The ICD for vegetable oils ranged from 31.2 to 1.7 (**Table 3**). Corn, peanut and

cottonseed showed the largest ICD while some of the variants of canola and sunflower oils gave ICD < 3 because of the subtle compositional differences among some of these oils. Mid-oleic sunflower and HO canola (II) showed the lowest ICD (1.7), followed by canola vs HO canola (I) (2.1), expeller-pressed sunflower vs HO canola (I) (2.3) and HO sunflower vs HO safflower (2.3), and mid-oleic sunflower vs HO canola (I) (2.6). The discriminating power plot provided important information regarding the functional groups responsible for the separation of oils into distinct oil classes and higher discriminating power values indicate greater influence of those wavenumbers in classifying the samples [23]. **Figure 3b** shows that most model variance was explained with bands at 1073 cm^{-1} corresponding to asymmetric stretching vibrations of ether groups [42], and the range of 2991 to 3047 cm^{-1} related to the C–H stretching vibrations of methyl and methylene groups and =C-H stretching vibrations of unsaturated aliphatic compounds associated to differences in the fatty acid chain length and degree of unsaturation among oils [22].

The predictive accuracy of the calibration model developed by portable FT-IR spectroscopy was evaluated using an independent external validation set that included 13 commercial samples. Assignments were correlated and confirmed with GC-FAME analysis results (**Table 2**). **Figure 4a** shows the SIMCA 3D projection plot for the validation set, while the predicted class assignments and manufacturer label information is presented in **Figure 4b**. Based on the manufacturer labeling information, 7 potato chip samples were processed with a sole type of oil including sunflower (HO, EP, regular, seed) and canola oils and 6 samples indicated the use of 1 or more type of oils. Our GC-FAME results showed that 8 out of 13 samples contained only one type of vegetable oil (ie. corn, sunflower, or canola) and 5 samples showed mixtures of oils based on their fatty acid profiles. All SIMCA predictions correlated with the GC-FAME assignments (**Figure 4b**) and showed 3 potato chip samples that had mislabeling of the oil

source. Sample **F**, which was labeled by the manufacturer as containing solely organic EP sunflower oil was clustered close to cottonseed oil and the GC-FAME results indicated that sample **F** includes cottonseed oil and at least one other type of oil. Sample **L** and **M**, same product from different lots, which were labeled as containing only sunflower oil, yet both samples clustered far from the sunflower oil at the SIMCA prediction plot and their GC-FAME confirmed it was an oil mixture. By combining the spectra collected using a portable IR sensor and pattern recognition analysis, a SIMCA classification allowed to rapidly (~1 min) identify the frying oils in potato chips and flagged potential mislabeling problems. The potential profits and trading advantages from mislabeling prejudice the interests of both consumers and honest manufacturers, and the use IR portable instruments would allow for efficient *in-situ* surveillance of high-value food ingredients such as vegetable oils.

3.2. Development of Predictive Models for Estimation of Major Quality Parameters

Partial least squares regression (PLSR) models were developed using the infrared spectra collected from a portable 5-bounce ATR unit and the reference values for fatty acid composition (GC-FAME) and rancidity tests (free fatty acids, peroxide value and *p*-anisidine). **Table 4** shows the performance statistics for the PLSR calibration and validation models obtained for the 5 major fatty (palmitic, stearic, oleic, linoleic and linolenic) acids, total saturated and polyunsaturated (PUFA) fatty acids in vegetable oils and the rancidity parameters. Two models were developed for linolenic acid based on their levels, group I include canola oils with levels ranging from 1.1 to 8.7% and group II included the rest of the oils ranging from 0.1 to 0.9%. The standard error of cross validation (SECV) determined from the calibration set using the leave-one-out approach and the standard error of prediction (SEP) using a validation set not included in the calibration model showed very similar values for the different components evidencing the

robustness of the prediction models. The SEP gave values ranging from 0.08 to 1.5% for the major fatty acids, 0.68% for the saturated and 0.91% for the polyunsaturated fatty acid present in the potato chip oil. **Figure 5** illustrates the very good correlations (R_{cal} 0.93 - 1) obtained between the infrared predicted values and the measured fatty acid composition by GC-FAME. Our performance statistics for the portable infrared unit was comparable to those reported using benchtop units and superior to a single-bounce handheld unit (**Table 1**).

Vegetable oils that contains high levels of polyunsaturated fatty acid are highly susceptible to hydrolysis, oxidation, and polymerization under frying environment [4]. Free fatty acids (FFA) generated by triacylglycerol hydrolysis upon release of water from the food being fried [43] have prooxidant action, exerted by the carboxylic molecular group, accelerating the rate of decomposition of hydroperoxides [44] and is an index used by the industry to monitor the quality of frying oil [4]. Our results showed that FFA levels ranged from 0.0 to 1.3% (**Table 4**) with an average of 0.33±0.2%, lower than the 1% FFA common industry criteria [45] and well below the 2% FFA maximum value set by the United States Department of Agriculture for discarding frying oil [46]. However, two samples out of 80 showed 3.5 and 8.4% FFA levels and were excluded from the PLSR model due to their high leverage. Most of the oils recovered from commercial potato chips evidenced very low hydrolytic rancidity in contrast to FFA levels reported in restaurant frying oils that showed an average of 0.93±1.03% FFA [46]. **Table 4** shows the performance statistics of the PLSR model developed for estimating FFA in oils using a portable FT-IR system. The calibration model gave high correlation coefficient (R_{cal} 0.97) and low standard error of prediction (SEP 0.07%) using 4 factors, and the RPD values for the model was 3.7 allowing for quality control applications. The 1750-1700 cm^{-1} spectral range was used to predict the FFA value with major bands centered at 1716 and 1746 cm^{-1} associated with carbonyl

bonds in acylglycerides and FFAs, respectively [47]. FFA quantification has been accomplished using the band height at 1716 cm^{-1} [19,47].

Peroxide value was used to monitor the formation of peroxides/hydroperoxides during the free radical reaction with oxygen [14], and as indicator of the frying oil freshness [8]. Peroxide value for the deep fat frying oils should be ≤1 meq/kg at the time of purchase [8], and oil with PV>10 meq/kg is considered rancid [48]. Our PV results ranged from 0.4 to 15.5 meq/kg (**Table 4**) with an average of 6.80±3.7 meq/kg. Fifteen samples out of 86 had PV above >10 meq/kg and two samples showed high PV levels (36.6 and 91.1 meq/kg) and were excluded from the models due to their high leverage. The PLSR model for estimating PV gave a SEP of 1.46 meq/kg and correlation coefficient (R) of 0.93, and similar model performances for peroxide values (1-20 meq/kg) have been reported in the literature (**Table 1**). **Figure 5** shows the correlation between measured and predicted values for PV using the spectral range between 1650-900 cm^{-1} and the regression vector showed that the important bands for predicting PV were centered at 1114 and 914 cm^{-1} associated with the formation of peroxy radical (O-O•) stretch between 1100 and 1200 cm^{-1} and the C-O• stretch at around 900 cm^{-1} [49,50].

Finally, *p*-Anisidine (*p*-AV) test was used to monitor secondary lipid oxidation products, aldehydes (especially 2,4-dienals and 2-alkenals), in frying oils [46,51]. *p*-AV is particularly useful to detect abused oils (e.g., deep-fat frying oils) with low PVs [52]. In our study, *p*-AV in oil extracted from potato chips ranged from 4.8 to 83.3 (**Table 4**) with an average of 34.97±20.8 *p*-AV, which are within the ranges reported in the literature for frying oils [46,53]. The PLSR models gave a SEP for the *p*-AV test of 4.11 and correlation coefficient of 0.96 using 3 factors with a RPD of 5.5 corresponding to a model suitable for quality control applications. The regression vector showed that the 1030-940 cm^{-1} spectral range was important in predicting the *p*-AV value

a major band centered at 980 cm^{-1} associated with δ RC=CH-HC=O vibration related with 2,4-decadienal compound [54].

4. CONCLUSION

Our data supports the application of a portable FT-IR spectrometer equipped with a 5-bounce ATR (ZnSe crystal) accessory and temperature control instrument for assessing potato chip oil quality in commercial potato chips. By using GC-FAME analysis, a total of 69 potato chip samples were manufactured with a single source of oil (ie. Canola, sunflower, corn, cottonseed, peanut, safflower or their high oleic variants). Combining the infrared spectra with pattern recognition analysis, potato chip oils were clustered based on the type of vegetable oil used for frying and a validation set showed 100% accurate predictions for the oils. Interestingly, we found 25% of the commercial potato chip samples had mislabeled information when reporting a single source of oil; these findings were supported by the GC-FAME analysis. Furthermore, the same spectra was used to develop PLSR models to estimate oil quality parameters showing strong correlations (Rval≥0.95) between reference tests and predicted values for major (palmitic, steraic, oleic, linoleic, and linolenic), saturated and polyunsaturated fatty acids, FFA, PV, and *p*-AV. Performance of the PLSR models are superior to models obtained from portable infrared systems in other studies, and also comparable to results from benchtop infrared systems. A portable spectrometer can provide the food industry with a rapid tool (~1 min) for oil screening and quality assurance applications that requires minimal sample preparation and personnel training and can be amenable for *in-plant* or *in-field* applications.

5. ACKNOWLEDGEMENTS

We are would like to thank Wyandot Snack Inc. to provide us vegetable oils. Finally, we would like to thank the Turkish Ministry of Education for supporting student fellowship at the Ohio State University.

Table 1 Performances and statistics of composition and degradation products of edible oils analyzed by MIR and NIR techniques.

Oil Sample	Analysis	Method	Multivariate Analysis	Results	Reference #
Crude palm	PV[c]	Transmittance NIR[f]	PLSR[m]	PV: 2.2-10.3meq/kg; SEP[o]=0.2	55
Palm olein		Transmittance FTIR[g]		PV: 3.5-9.9meq/kg; SEP=0.2	56
Canola		FT-NIR[h]		PV: 0-15.1meq/kg; R[p]=0.98	57
Soybean, palm kernel olein		HATR-FTIR[i]		PV: 4-45meq/kg; RMSECV[q]=2.1	58
Canola, safflower, peanut, cottonseed, corn, sunflower		3-bounce ATR-MIR[j]		PV: 1-20meq/kg; SECV[r]=1	23
		1-bounce ATR-MIR (portable)		PV: 1-20meq/kg; SECV=1	
Virgin coconut		ATR-FTIR[k]		RMSEP[s]=0.5	59
Virgin olive		ATR-FTIR		PV: 5.7-15.7 meq/kg; RMSD[t]=0.7	60
Virgin olive		ATR-FTIR		PV: 11.1-49.7meq/kg; RMSECV=4	47
Corn, HO sunflower[a], flax, sacha inchi		ATR-FTIR (benchtop)		PV: 1-66 meq/kg; SECV=2.1	22
		ATR-FTIR (portable)		PV: 1-66 meq/kg; SECV=5	
Frying oil	FFA[d]	NIR	PLSR	FFA: 0-0.6%; RPD[u]=2.5	61
Crude palm		Reflectance NIR	MLR[n]	FFA: 3.5-6.2; RMSEP=0.1	62
Palm olein		Transmission FTIR	PLSR	FFA: 0.1-1%; SEP=0	63
Virgin olive		ATR-FTIR		FFA: 0.2-9.2%; RMSECV=0.2	47
Corn, HO sunflower, flax, sacha inchi		ATR-FTIR (benchtop)		FFA: 0-1%; SECV=0.1	22
		ATR-FTIR (portable)		FFA: 0-1%; SECV=0.1	
Soybean oil	*p*-AV[e]	Transmission NIR	PLSR	*p*-AV: 0.5-1.8; SEP=0.6	64
Palm olein		Transmission FTIR		*p*-AV: 0.1-17.1; SEP=0.5	63
Canola, safflower, peanut, cottonseed, corn, sunflower	Fatty acid profile	3-bounce ATR-MIR (benchtop)	PLSR	Saturated: 5.9-28.5%; SECV=0.2 PUFA[v]: 13.1-57.8%; SECV=0.6	23
		1-bounce ATR-MIR (portable)		Saturated: 5.9-28.5; SECV=1.1 PUFA: 13.1-57.8; SECV=2.2	
Palm, sunflower, soybean, canola, cottonseed, rice bran, PHO[b]		SB-ATR[l], FTIR		PUFA: 1.2-64.3%; RMSEP=1.2	65
Corn, HO sunflower, flax, sacha inchi		ATR-FTIR (benchtop)		Oleic: 9.6-76.6%; SECV=2	22
		ATR-FTIR (portable)		Oleic: 10.6-78.6%; SECV=2.7	
		ATR-FTIR (benchtop)		Linoleic: 7.4-56%; SECV=1.1	
		ATR-FTIR (portable)		Linoleic: 8.4-56%; SECV=2.7	

[a]High oleic sunflower, [b]Partially hydrogenated oil, [c]Peroxide value, [d]Free fatty acids, [e]*p*-anisidinde value, [f]Near infrared, [g]Fourier transform infrared, [h]Fourier transform near infrared, [i]Horizontal attenuated total reflectance Fourier transform infrared, [j]Attenuated total reflectance mid infrared, [k]Attenuated total reflectance Fourier transform infrared, [l]Single bounce attenuated total reflectance, [m]Partial least squares regression, [n]Multiple linear regression, [o]Standard error of prediction, [p]Correlation coefficient , [q]Root mean square error of cross validation, [r]Standard error of cross validation, [s]Root mean square error of prediction, [t]Root mean square deviation, [u] Residual predictive deviation, [v] Polyunsaturated fatty acids.

Table 2 Fatty acid composition (%) for potato chips oil samples using fatty acid methyl ester (FAME) procedure.

Sample	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Corn	12±1	2±0	28±1	57±1	1±0
Canola	5±0	2±0	65±1	20±0	7±1
HO Canola (I)[a]	4±0	2±0	68±0	23±0	3±0
HO Canola (II)[b]	4±0	2±0	74±2	17±2	2±0
Peanut	11±0	3±0	58±1	27±1	0±0
HO Sunflower[c]	5±1	3±0	80±3	12±2	0±0
HO Safflower[d]	6±1	2±0	76±1	16±0	0±0
MO Sunflower[e]	5±0	4±0	65±1	26±2	0±0
Cottonseed	24±1	2±0	17±1	57±2	0±0
EP Sunflower[f]	6±1.2	3±0.7	61±1.4	30±2.1	0±0

[a]High oleic canola (I), [b]High oleic canola (II), [c]High oleic sunflower, [d]High oleic safflower, [e]Mid oleic sunflower, [f]Expeller pressed sunflower.

Table 3 Interclass distances between 10 potato chip frying oils based on SIMCA class projections of the FT-IR spectra collected at the 700-4000 cm^{-1} region.

Groups[a]	1	2	3	4	5	6	7	8	9	10
1	0.0									
2	14.1	0.0								
3	15.4	2.1	0.0							
4	18.7	8.0	6.9	0.0						
5	21.2	5.1	2.6	4.9	0.0					
6	5.3	14.7	13.5	13.5	17.6	0.0				
7	25.0	6.5	3.8	5.2	1.7	22.8	0.0			
8	19.0	4.1	2.3	6.6	3.0	18.5	5.2	0.0		
9	28.1	10.1	7.0	2.3	5.0	23.7	5.1	9.3	0.0	
10	31.2	15.4	13.8	5.3	12.2	21.9	15.4	20.0	12.2	0.0

Groups[a] 1: Corn, 2: Canola, 3: High Oleic Canola (I), 4: High Oleic Sunflower, 5: Mid Oleic Sunflower, 6: Cottonseed, 7: High Oleic Canola (II), 8: Expeller Pressed Sunflower, 9: High Oleic Safflower, 10: Peanut

Table 4 Performance of calibration and validation models developed by using portable FT-IR instrument for estimating palmitic, stearic, oleic, linoleic, linolenic, saturated, PUFA, FFA, PV, and *p*-AV levels in potato chips samples.

	Calibration model					Validation model				
	Range	n[a]	Factor	SECV[b]	r Cal	Range	n	SEP[c]	r Val	RPD[d]
Palmitic (%)	3.6-25.0	73	4	0.78	0.99	4.0-21.1	18	0.84	0.99	5.4
Stearic (%)	1.4-3.9	70	4	0.29	0.93	1.5-3.7	18	0.22	0.97	3.8
Oleic (%)	14.9-85.6	73	4	1.68	1.00	25.2-82.8	18	1.51	1.00	13.3
Linoleic (%)	7.3-65.0	76	4	1.50	1.00	10.3-58.2	19	1.00	1.00	16.5
Linolenic I (%)	1.1-8.7	25	5	0.35	0.99	NA[g]	NA	NA	NA	NA
Linolenic II (%)	0.1-0.9	47	3	0.09	0.96	0.1-0.9	12	0.08	0.96	3.6
Saturated[e] (%)	5.8-27.8	73	4	0.75	0.99	6.6-23.9	18	0.68	0.99	6.3
PUFA[f] (%)	7.6-65.1	76	4	1.26	1.00	10.7-59.0	19	0.91	1.00	18.1
FFA (%)	0.0-1.3	64	4	0.05	0.97	0.1-1.0	16	0.07	0.96	3.7
PV (meq/kg)	0.4-15.5	69	4	1.27	0.93	2.0-15.5	17	1.46	0.95	2.8
p-AV	4.8-83.3	68	3	5.94	0.96	6.3-76.5	17	4.11	0.98	5.5

[a]Number of samples, [b]Standard error of cross validation, [c]Standard error of prediction, [d]Residual predictive deviation, [e]Saturated fatty acids, refers to the total concentration of palmitic and stearic acids, [f]Polyunsaturated fatty acids, refers to the total concentration of linoleic and linolenic acids, [g]Validation model was not generated for Linolenic I due to its low number of samples (n=25).

LIST OF FIGURES

Figure 1. **(a)** Demonstration of typical spectrum collection using a portable FT-IR spectrometer equipped with a 5-bounce heated ZnSe crystal. **(b)** Demonstration of FT-IR spectrometer screen obtained when an unknown potato chip oil sample is deposited onto the crystal and all quality parameters are predicted.

Figure 2. **(a)** FT-IR spectrum and band assignments of vegetable oils collected using a 5-bounce Zn Se crystal ATR system equipped with a temperature-controlled accessory. **(b)** Second derivative of the spectrum transformations for the corresponding vegetable oils.

Figure 3. **(a)** Soft independent modeling of class analogy (SIMCA) 3D projection plots of second derivative-transformed spectral data collected by portable FT-IR spectrometer for frying oils extracted from commercial potato chips. For SIMCA plots, boundaries marked around the sample-clustered represents a 95% confidence interval for each class. Whether the residual variance of a sample exceeds the boundary limit for the modeled class in the data set, it was not assigned to any of the classes; either assigned as an outlier or belongs to a class not represented in the data set. **(b)** SIMCA discriminating plot based on the mid-infrared spectra of oils using a portable FT-IR spectrometer, showing bands and regions responsible for class separation.

Figure 4. **(a)** SIMCA class projections for the external validation set, letters from **A** to **M** represent each validation set samples. The ellipses represent the class boundaries for the vegetable oils (n=10) used in the calibration set. Class numbers represent vegetable oil groups as followed; **1**: High oleic sunflower, **2**: High oleic safflower, **3**: Peanut, **4**: Mid oleic sunflower, **5**: High oleic canola (II), **6**: Expeller pressed sunflower, **7**: High oleic canola (I), **8**: Canola, **9**:

Cottonseed, **10**: Corn **(b)** Manufacturer's label claims, GC-FAME assignments and SIMCA predictions for external validation set.

Figure 5. Partial least squares regression (PLSR) calibration and validation plots for palmitic (1030-1150, 2790-3000 cm^{-1})* **(a)**, oleic (1030-1170, 3000-3060 cm^{-1}) **(b)**, linoleic (1040-1120 cm^{-1}) **(c)**, free fatty acids (1700-1750 cm^{-1}) **(d)**, peroxide value (900-1650 cm^{-1}) **(e)**, *p*-anisidine (940-1030 cm^{-1}) **(f),** saturated fatty acid (900-1210, 2766-3000 cm^{-1}) **(g)**, and polyunsaturated fatty acid (1045-1125, 2876-3055 cm^{-1}) **(h)** levels in potato chips samples using portable FT-IR instrument. Grey squares represent samples in calibration groups; black squares represent samples in validation groups. *The part of the Mid-IR region used for the models.

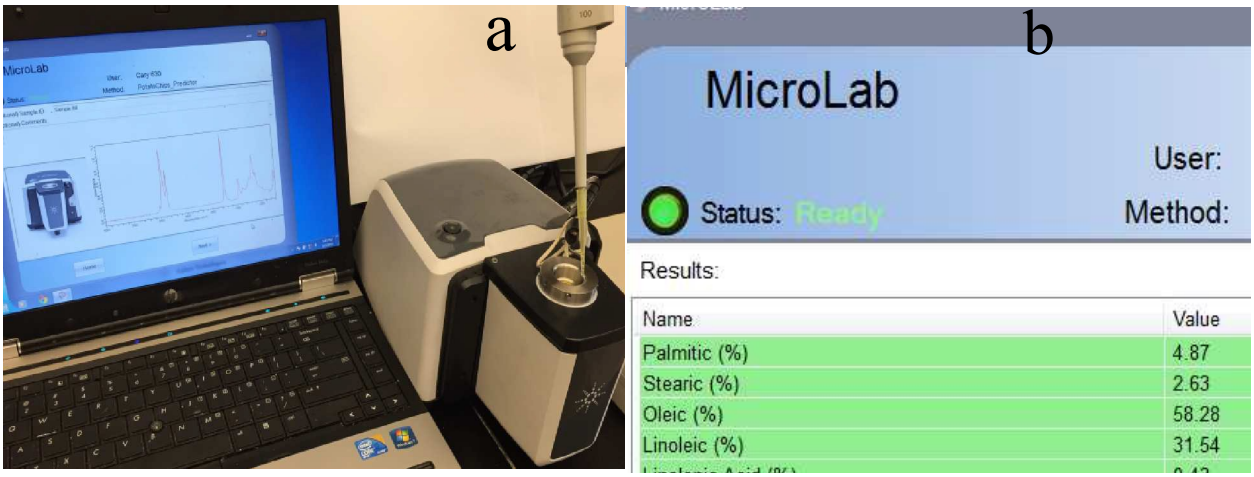


Figure 1.

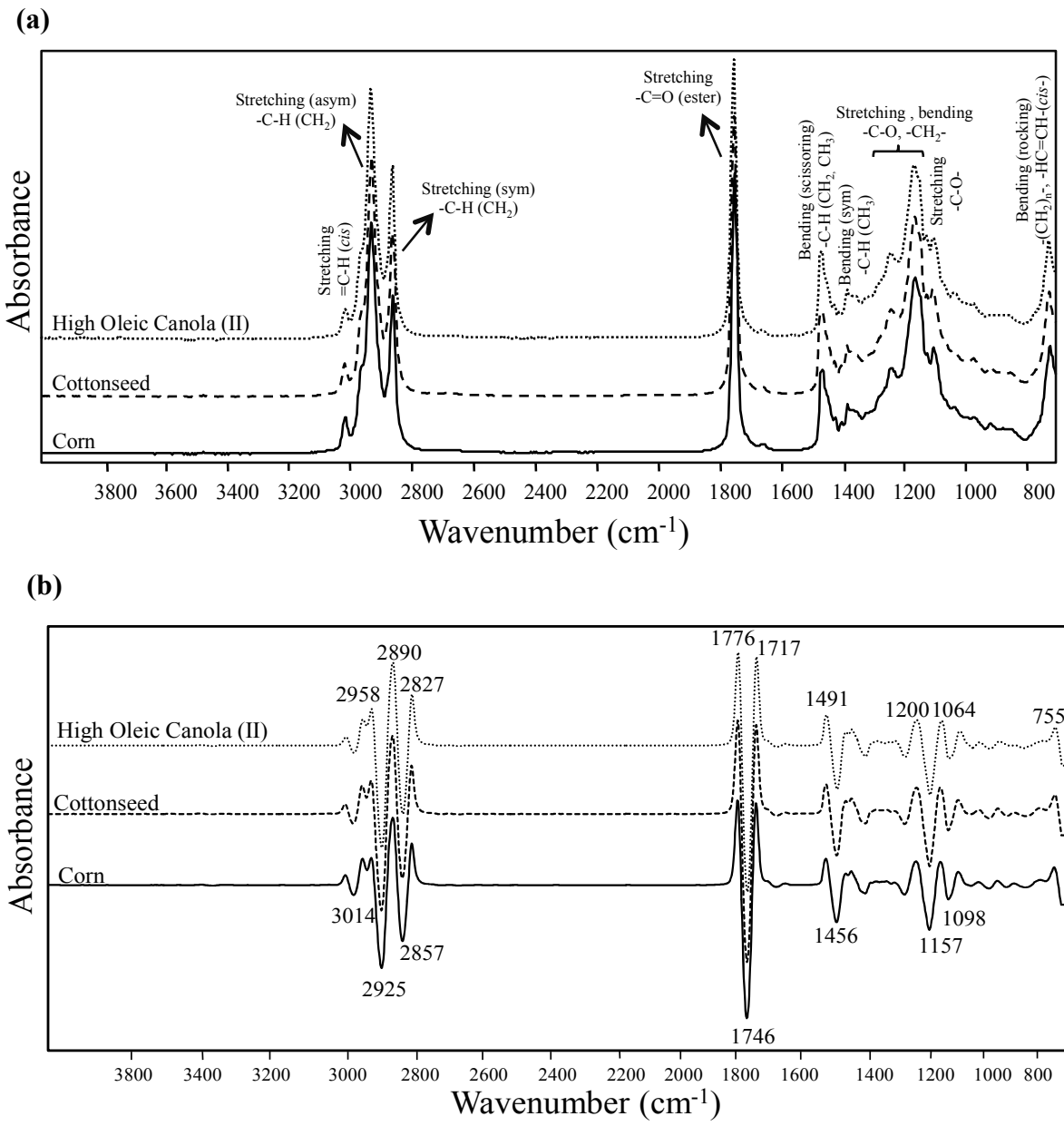


Figure 2.

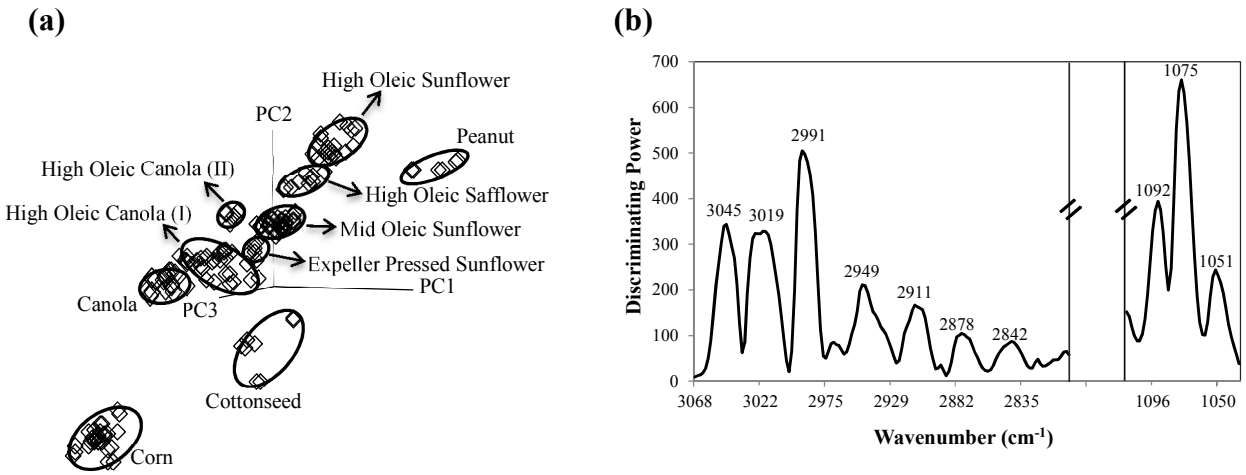
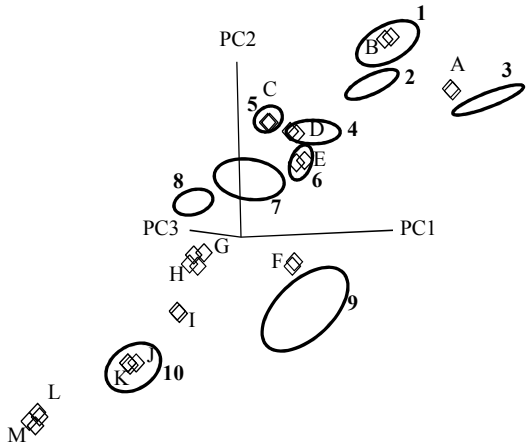


Figure 3.

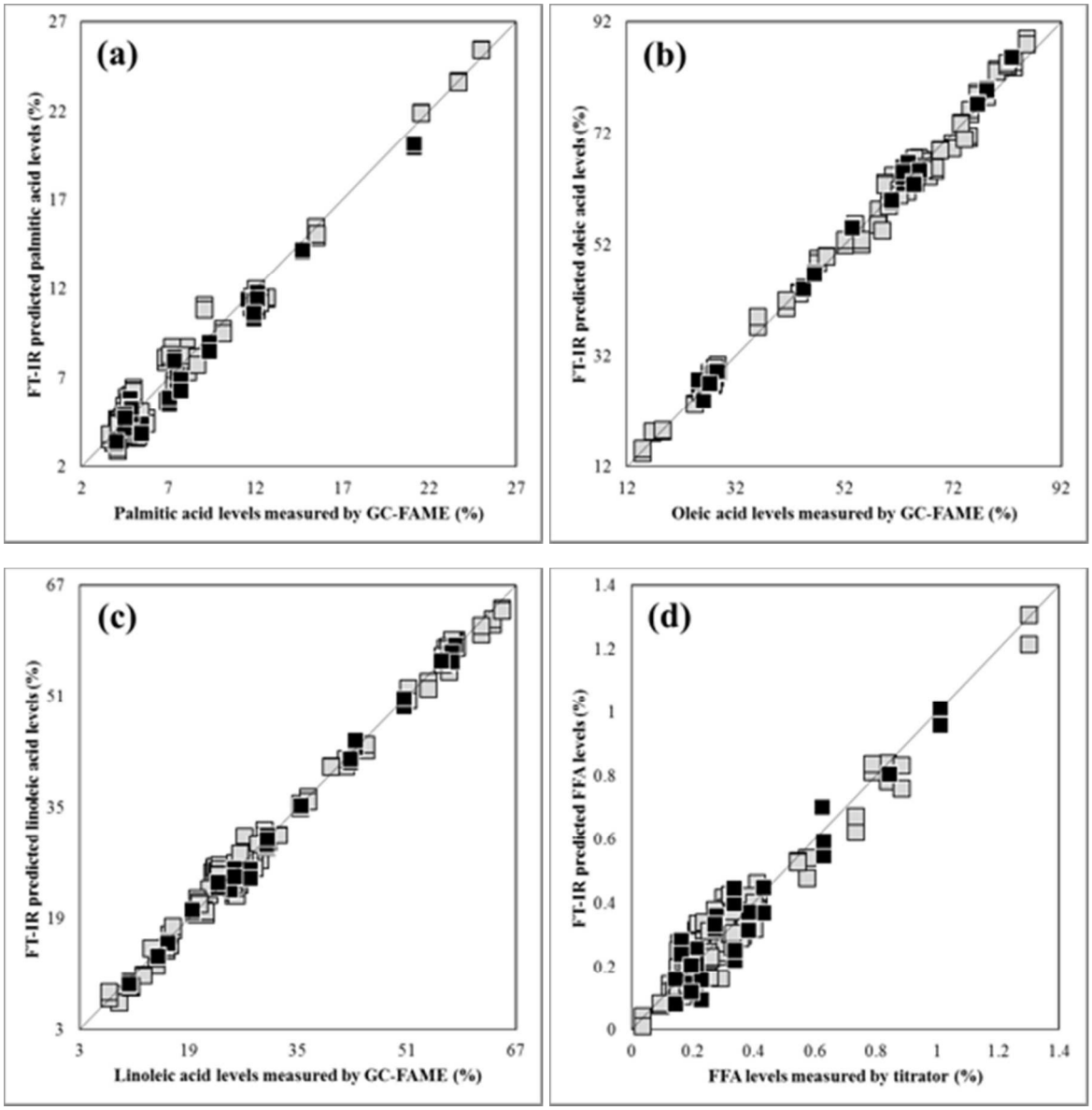
(a)



(b)

Sample	Label	GC-FAME Assignment	SIMCA Prediction
A	Cottonseed, Peanut, Sunflower, Safflower, Canola a/o Corn	Mixture (main component peanut)	Mixture
B	HO Sunflower	HO Sunflower	HO Sunflower
C	Canola	HO Canola (II)	HO Canola (II)
D	Sunflower seed	MO Sunflower	MO Sunflower
E	EP Sunflower	EP Sunflower	EP Sunflower
F	Organic EP Sunflower	Mixture (main component cottonseed)	Mixture
G	Sunflower, Corn a/o Canola	Mixture	Mixture
H	Sunflower, Corn a/o Canola	Mixture	Mixture
I	Sunflower seed a/o EP Corn	Mixture (main component corn)	Mixture
J	Corn, Soybean a/o Sunflower	Corn	Corn
K	Corn, Peanut, Cottonseed, Soybean a/o Sunflower	Corn	Corn
L	Sunflower	Mixture	Mixture
M	Sunflower	Mixture	Mixture

Figure 4.



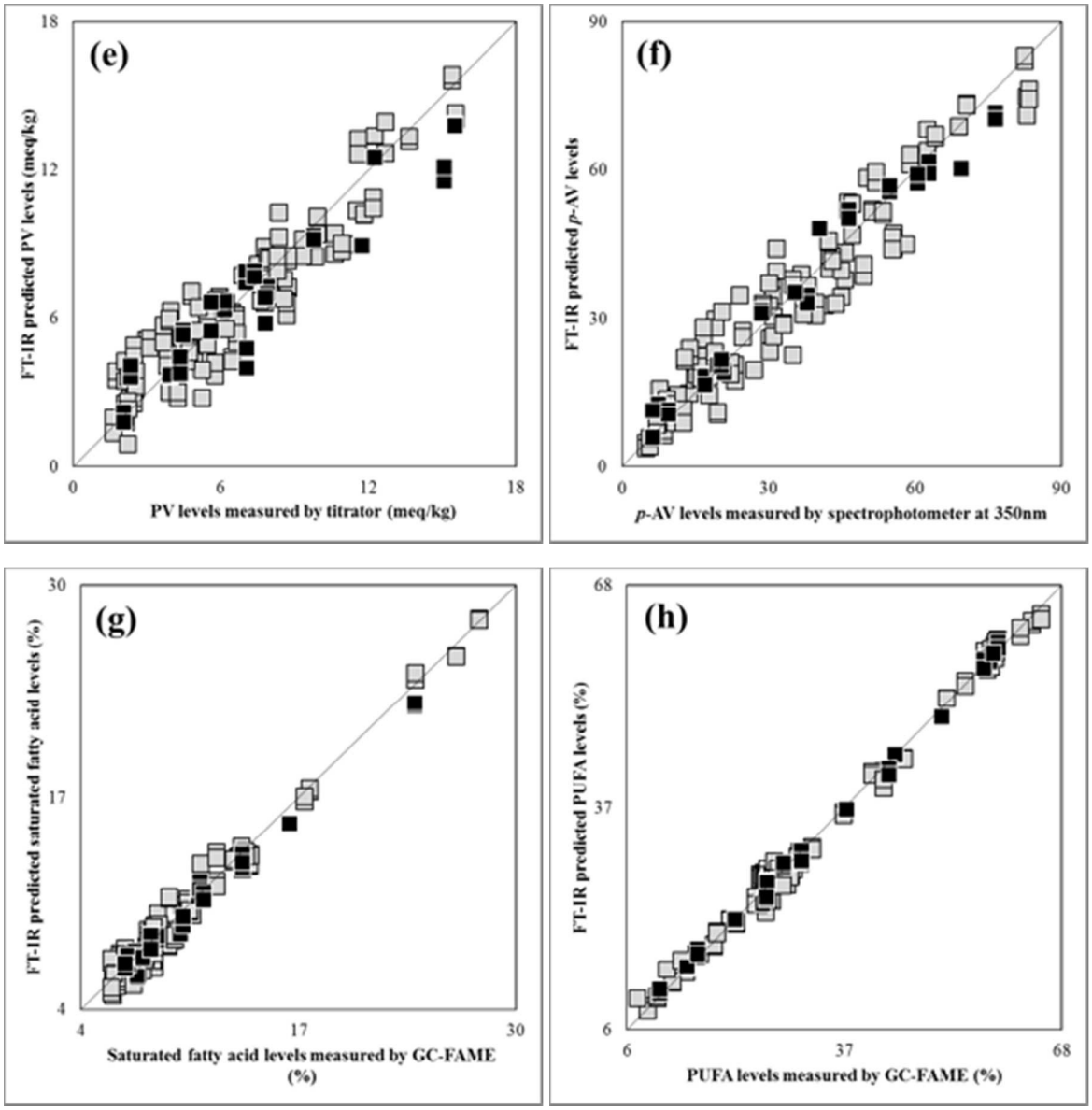


Figure 5.

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