

## Article

# Determination of the Acidity of Waste Cooking Oils by Near Infrared Spectroscopy

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**Abstract:** Waste cooking oils (WCO) recycling companies usually have economic losses for buying WCO not suitable for biodiesel production, e.g., WCO with high free acidity (FA). For this reason, the determination of FA of WCO by near infrared (NIR) spectroscopy was studied in this work to assess its potential for in situ application. To do this, FA of 45 WCO was measured by the classical titration method, which ranged between 0.15 and 3.77%. Then, the NIR spectra from 800 to 2200 nm of these WCO were acquired, and a partial least squares model was built, relating the NIR spectra to FA values. The accuracy of the model was quite high, providing  $r^2$  of 0.970 and a ratio of performance to deviation (RPD) of 4.05. Subsequently, a model using an NIR range similar to that provided by portable NIR spectrometers (950–1650 nm) was built. The performance was lower ( $r^2 = 0.905$ ; RPD = 2.66), but even so, with good accuracy, which demonstrates the potential of NIR spectroscopy for the in situ determination of FA of WCO.

**Keywords:** free acidity; NIRS; partial least squares; waste cooking oil

## 1. Introduction

Fossil fuel combustion has negative effects on the environment. Therefore, current research is mainly focused on the search for economic, environmentally friendly biofuels that can replace petroleum fuels. Diesel combustion in engines leads to air pollution by greenhouse gas emissions, namely  $\text{NO}_x$ , CO, and  $\text{CO}_2$ , and to the destruction of the ozone layer, due to photochemical interactions of the hydrocarbon, CO, and  $\text{NO}_x$  emissions. As an alternative to petroleum diesel fuel, the currently produced biofuel is biodiesel, which is composed of fatty acid methyl esters (FAME). Biodiesel is obtained by transesterification of vegetable oils with short-chain alcohols, mainly methanol [1].

The main problems of biodiesel production from vegetable oils are the high cost of the raw materials, the threat to food security [2,3], and the oversupply of glycerin as a byproduct [4]. The current alternative to vegetable oils is the use of waste cooking oils (WCO) as raw material for biodiesel production. WCO are much cheaper than vegetable oils from crops or trees, are not in conflict with food security, and are available as waste products [3,5]. The HORECA (hotels, restaurants, and catering) sector produces roughly 400,000 tons of WCO per year in Spain [3]. As a profitable market, many enterprises dealing with the collection and recycling of waste cooking oils for subsequent biodiesel production have been set up [6].

Frying consists of introducing food to an oil bath at temperatures between 160 and 200 °C, during a certain period in the presence of air. Because of this high temperature exposure, the oil undergoes numerous physical and chemical changes that make the characteristics of this oil different. Among these changes, the most notorious one is the increasing of acidity, mainly provoked by the release of free fatty acids from the partial hydrolysis of triglycerides.

WCO recycling companies usually collect these oils from clean points or special containers, or buy entire trucks from smaller companies. After filtering in their facilities to remove leftover food, flour, etc., WCO are left to decant to obtain three phases: Clean oil, water, and sludge [6]. This oil is then analysed. The main requirement is that the free acidity (FA) is lower than 2.5%. If not, in order to be suitable for biodiesel production, this oil must be subjected to a chemical process (esterification) to reduce FA. Most WCO recycling companies usually do not have either reactors nor qualified staff to carry out the esterification reaction, so these companies have to sell this oil to bigger companies that have the required equipment (mainly biodiesel producers) at a lower price than that of purchase, or to pay to an environmental manager to dispose it. This problem could be overcome if FA was measured in situ. The determination of oil FA is carried out by acid–base titration, and cannot be performed in situ because it needs reagents, sample preparation, and laboratory glassware, and generates chemical wastes.

Near-infrared spectroscopy (NIRS) is a low-cost, safe, and non-destructive technique, which generally does not require sample preparation or chemicals [7,8]. Nowadays, portable near-infrared spectrometers can be purchased for roughly 6000 € (e.g., Oceanoptics Flame-NIR Spectrometer). Therefore, NIRS can be suitable for in situ analysis. The potential of NIRS for olive and sunflower oils' free acidity determination has been demonstrated [7–9], which makes it feasible that WCO's FA can also be measured by NIRS.

The aim of this work is to assess the feasibility of determining the free acidity of waste cooking oils by near-infrared spectroscopy and verify whether this technique can be used for its in situ determination by WCO collection and recycling companies. To do this, FA determination in WCO was first assayed using the whole NIR spectrum. Subsequently, it was assayed in a reduced NIR interval, similar to that provided by portable NIR spectrometers, thus proving the applicability of the technique.

## 2. Materials and Methods

### 2.1. Waste Cooking Oils (WCO)

Fifty WCO were collected from the university canteen of the Reina Mercedes Campus (University of Seville) and different private households. These WCO were olive, sunflower and pomace oils, and mixtures of them. This ensured a wide variety of oil types and degradation degrees. Once received at the laboratory, WCO were filtered to remove solids such as leftover food, flour, etc.

### 2.2. Free Acidity (FA) Determination by Acid–Base Titration

The percentage of free fatty acids that WCO contain, expressed as oleic acid percentage, was measured according to the Official Methods of Analysis of the EC [10,11]. Briefly, 20 g WCO were placed into 250-cm<sup>3</sup> wide-mouth Erlenmeyer flasks along with 50 cm<sup>3</sup> ethanol/ethyl ether solution (1:1 v/v) and a few drops of phenolphthalein, and then neutralized with 0.1 N KOH, previously standardized with benzoic acid. The titration ends when a reddish-brown color change is observed. Determinations were performed in duplicate.

The percentage of acidity of the oil was calculated according to the following equation:

$$\text{FA (\%)} = \frac{V \times 0.1 \text{ N} \times 0.282}{m} \times 100$$

where V is the spent volume of KOH in mL, 0.1 N stands for the KOH normality, 0.282 is the equivalent weight of oleic acid in mequiv, and m is the mass of WCO sample in grams. The FA contents ranged between 0.15% and 3.77%, being the mean value and standard deviation, 0.94% and 0.79%, respectively.

### 2.3. Spectra Acquisition

Before spectra acquisition, WCO samples were kept at 32 °C for 30 min in a water bath because NIR radiation reflected and absorbed by a sample depends on its temperature and this temperature ensures that all oil compounds are completely dissolved. A Vis/NIR Labspec Pro model LSP 350-2500P (Analytical Spectral Devices Inc., Boulder, CO, USA) spectrophotometer with three detectors was used for spectral acquisition, as described in [7]. The spectrophotometer is equipped with internal shutters and automatic offset correction, the scanning speed time being 100 ms.

Samples were introduced in a 10-mm quartz cuvette, which was placed in a cuvette accessory joined by fibre optic connectors to the spectrophotometer light source on one side, and to the spectrophotometer detector on the opposite side. This optical path length was selected because it showed higher absorption intensity than 1 mm, 2 mm, and 5 mm path-length quartz cuvettes when acquiring olive oil NIR spectra [7]. NIR spectra from 800 to 2200 nm were then acquired in transmittance mode and recorded using the Indico Pro software (Analytical Spectral Devices Inc. Boulder, CO, USA), each spectral variable matching to a 1-nm interval. The spectrum of each sample was acquired in duplicate.

### 2.4. Calibration Procedure and Model Evaluation

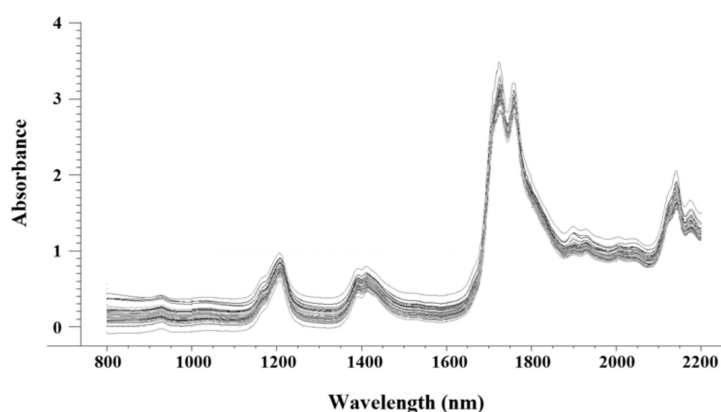
Reflectance data were first transformed to absorbance and then maximum normalised. Partial least squares (PLS) models coupled to full-cross internal validation were built with The Unscrambler software (CAMO Software AS, Oslo, Norway) for the full NIR spectrum (800–2200 nm) and for the wavelength interval specified for the Ocean Optics Flame-NIR spectrometer (950–1650 nm).

The standard error of calibration (SEC) and the multiple correlation coefficient of calibration ( $r^2_c$ ) were used to assess models' fitness. The prediction performance of the models was evaluated based on the standard error of prediction (SEP), which corresponds to the standard error of full-cross validation, the multiple correlation coefficient of full-cross validation ( $r^2_{cv}$ ), and the ratio of performance to deviation (RPD). The RPD was defined as the ratio between the standard deviation from the FA reference data and SEP. Among them, the most important parameters to assess the performance of a PLS model are  $r^2_c$  (calibration) and RPD (validation): The higher these parameters are, the higher the accuracy of the model. To be specific, models with  $r^2_c \geq 0.90$  are considered to have excellent precision, while models with  $r^2_c = 0.70$ – $0.89$  are regarded as good precision models [12]. As for RPD, this parameter must be higher than 3 for a PLS model to be considered of excellent precision [13], although another author has pointed out that predictive models suitable for routine analysis should have RPD values between 2 and 10 [14].

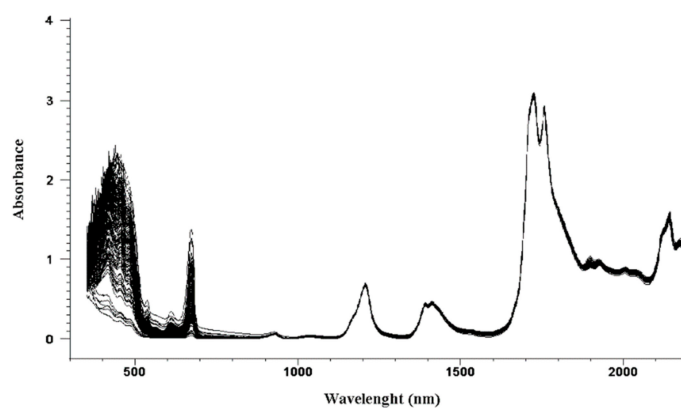
## 3. Results

### 3.1. Features of the NIR Spectra of Waste Cooking Oils

Absorbance in the NIR region is linear with the concentration of organic compounds. The NIR spectrum of a sample consists of first and second overtones (800–1800 nm) and combination bands (1800–2700 nm) of fundamental, largely hydrogenic vibrations that occur in the MIR region. The acquired WCO absorbance spectra (Figure 1) were practically identical to those previously obtained for olive oils (Figure 2), so their main features are described elsewhere [7]. Briefly, from left to right, a broad absorbance band is observed at 1210 nm, which is related to C–H second overtones and CH=CH–stretching vibrations. Next, a wide absorption band, due to the water first overtone, is observed in the 1350–1450 nm region. The intense absorption found at 1720 nm is related to the first overtone of the C–H vibration of several chemical groups (=CH–, –CH<sub>3</sub>, –CH<sub>2</sub>–) and is characteristic of triglycerides and fatty acids of vegetable oils [7]. Another broad water combination band is located at 1880–2100 nm. The two water bands (1350–1450 nm and 1880–2100 nm) show multiple overlapping bands. Finally, the absorption band of the C–H vibration of cis-unsaturation occurs at 2140 nm.



**Figure 1.** Near-infrared spectra of the waste cooking oils (WCO) used in this research.



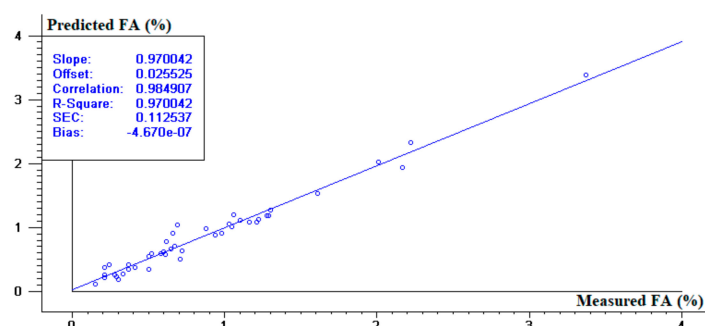
**Figure 2.** Visible/near-infrared spectra of olive oils [7].

### 3.2. NIR Partial Least Squares Model for the 800–2200 nm Spectrum

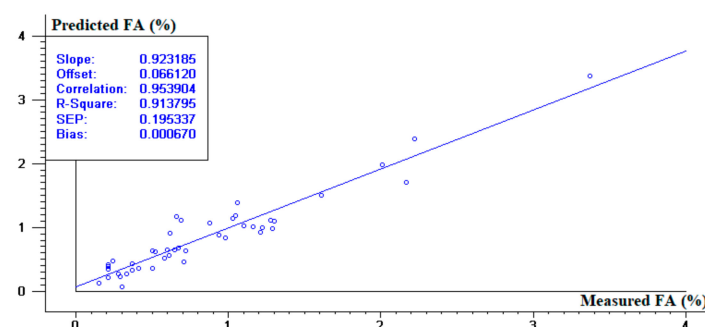
In light of the similarity between the NIR spectra of vegetable and waste cooking oils, it is reasonable to think that free acidity of WCO can be obtained from their NIR spectra, as it has been demonstrated for olive oil [7,8]. Indeed, the PLS calibration model for FA determination, built using the 800–2200 NIR absorbance spectra of the 45 WCO samples, achieved high  $r^2_c$  and RPD (0.970 and 4.05, respectively), which accounts for the excellent precision of the model taking into account the aforementioned criteria [12–14]. Figures 3 and 4 illustrate the fit of the data to the proposed model, along with the model statistics. The number of optimal principal components to build this PLS model was nine, explaining 95.1% of the variation in the FA data. Models with large total explained variance (close to 100%) explain most of the variation in the data. Ideally, in order to have simple models, the residual variance has to go down to zero with as few principal components as possible. If this were not the case, it would mean that there might be a large amount of noise in the data.

### 3.3. NIR Partial Least Squares Model for the 950–1650 nm Spectrum

Once it was proved the NIRS was suitable to determine FA in WCO, the second objective of this work was to try to quantify FA in WCO using a narrower NIR range, similar to the typical range provided by portable NIR spectrometers. In this case, the selected range was 950–1650 nm. The PLS model was built using nine principal components, which explained 90.5% of the variation in the FA data. According to the criteria established [12–14], this PLS model can be regarded as a good precision model. As shown in Figure 5, the statistics of the calibration model were satisfactory, achieving an acceptable  $r^2_c$  (0.90). However, SEP increased to 0.30% (Figure 6), thus decreasing the RPD value to 2.66. Compared to the model obtained for the 800–2200 nm NIR range, the precision of the model obtained for 950–1650 nm is markedly lower (Table 1).



**Figure 3.** Performance of the 800–2200 partial least squares (PLS) model for free acidity (FA) determination.

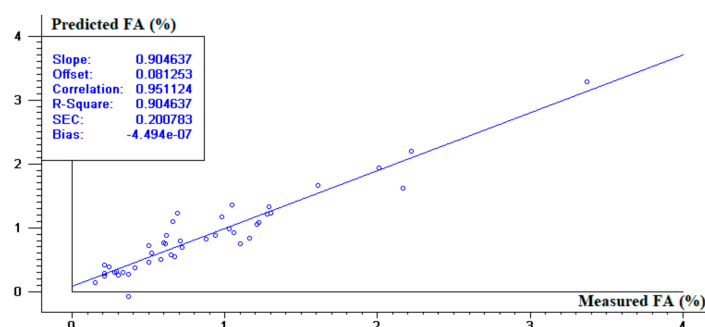


**Figure 4.** Validation of the 800–2200 PLS model for FA determination.

**Table 1.** Statistics of the PLS models obtained for the two assayed near-infrared spectroscopy (NIRS) intervals.

NIR Interval	n	$r^2_c$	$r^2_{cv}$	SEC	SEP	RPD
800–2200	1401	0.970	0.914	0.113	0.195	4.05
950–1650	701	0.905	0.800	0.201	0.297	2.66

n: Spectral variable number;  $r^2_c$ : Correlation coefficient of calibration; SEC: Standard error of calibration; SEP: Standard error of prediction; RPD: Ratio of performance to deviation.



**Figure 5.** Performance of the 950–1650 PLS model for FA determination.

This could be due to the missing information related to the first overtone of the C–H vibration of several chemical groups ( $=CH-$ ,  $-CH_3$ ,  $-CH_2-$ ), characteristic of fatty acids of vegetable oils, which was found to be 1720 nm. That aside, WCO contain not only the vegetable oil components, but also degradation products, due to thermal, oxidative, and hydrolytic reactions that occur during frying and food rests (flour, etc.). These components differ among samples and can decrease the PLS model performance. Their negative effect can be balanced, increasing the number of contributing spectral

variables to the model, which accounts for the higher accuracy of the PLS model built for the NIR range 800–2200 nm. The precision of both PLS models could be improved, eliminating spectral variables without information related to the measured parameter, such as noise and background, or removing outliers in the calibration and validation sets [7]. However, the accuracy of the 950–1650 nm PLS model is enough for the proposed purpose: The in situ determination of FA of WCO. In fact, the achieved SEP is not high when compared to other authors' results. In this sense, the SEP using the whole NIR spectrum (from 750 to 2500 nm) was 0.35% for virgin olive oils [8], while in this work, the SEP for waste cooking oils was 0.30%. Furthermore, the use of techniques for uninformative spectral variable removing requires knowledge in programs such as MATLAB (The MathWorks, Inc., Natick, MA, USA), and the purchase of these programs and powerful computers, which will obviously decrease the feasibility and practical application of NIRS to in situ FA determination.

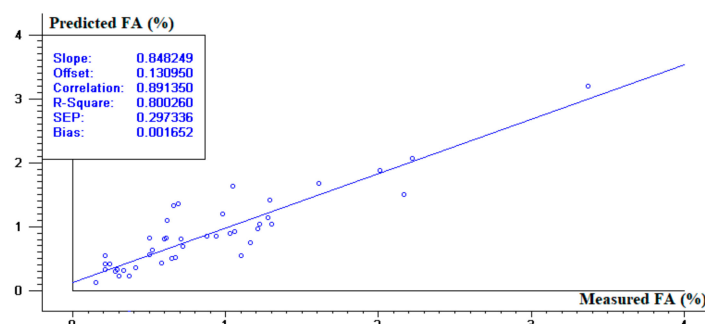


Figure 6. Validation of the 950–1650 PLS model for FA determination.

#### 4. Conclusions

In the absence of tests at companies' facilities with different portable NIR spectrometers, the potential of near-infrared spectroscopy for in situ waste cooking oils' free acidity determination has been demonstrated. High accuracy was achieved when using the whole NIR range provided by a benchtop NIR spectrometer ( $r^2 = 0.970$ ; RPD = 4.05). Although not perfect, the accuracy of the partial least squares model, built using a wavelength range similar to that incorporated in portable NIR spectrometers (950–1650 nm), was good ( $r^2 = 0.905$ ; RPD = 2.66). Furthermore, the standard error of prediction achieved with this narrow NIR interval (0.30%) was in the range of that obtained by other authors for vegetable oils using the full NIR spectrum, which accounts for the ability of NIR spectroscopy to determine free acidity of waste cooking oils.

**Author Contributions:** Conceptualization, J.F.G.-M.; methodology, J.F.G.-M. and P.Á.-M.; formal analysis, J.F.G.-M. and Q.-A.Z.; investigation, M.d.C.L.-B.; data curation, M.d.C.L.-B. and P.Á.-M.; software, M.d.C.L.-B. and J.F.G.-M.; writing—original draft preparation, J.F.G.-M.; writing—review and editing, J.F.G.-M.; supervision, J.F.G.-M. and P.Á.-M.; project administration, P.Á.-M.; funding acquisition, P.Á.-M. and M.T.-G.

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**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Pereda Marín, J.; Barriga Mateos, F.; Álvarez Mateos, P. Aprovechamiento de las oleinas residuales procedentes del proceso de refinado de los aceites vegetales comestibles, para la fabricación de biodiesel. *Grasas y Aceites* **2003**, *54*, 130–137.
2. Sánchez, S.; Cuevas, M.; García-Martín, J.F. Bioethanol production: Corn v/s lignocellulose biomass from olive oil industry and the potential role in ensuring food security. *J. Fundam. Renew. Energy Appl.* **2015**, *5*, 18.
3. García-Martín, J.F.; Barrios, C.C.; Alés-Álvarez, F.J.; Dominguez-Sáez, A.; Alvarez-Mateos, P. Biodiesel production from waste cooking oil in an oscillatory flow reactor. Performance as a fuel on a TDI diesel engine. *Renew. Energy* **2018**, *125*, 546–556. [[CrossRef](#)]



4. García-Martín, J.F.; Alés-Álvarez, F.J.; Torres-García, M.; Feng, C.-H.; Álvarez-Mateos, P. Production of Oxygenated Fuel Additives from Residual Glycerine Using Biocatalysts Obtained from Heavy-Metal-Contaminated *Jatropha curcas* L. Roots. *Energies* **2019**, *12*, 740. [\[CrossRef\]](#)
5. García-Martín, J.F.; Alés-Álvarez, F.J.; del Carmen López-Barrera, M.; Martín-Domínguez, I.; Álvarez-Mateos, P. Cetane number prediction of waste cooking oil-derived biodiesel prior to transesterification reaction using near infrared spectroscopy. *Fuel* **2019**, *240*, 10–15. [\[CrossRef\]](#)
6. Álvarez-Mateos, P.; García-Martín, J.F.; Guerrero-Vacas, F.J.; Naranjo-Calderón, C.; Barrios, C.C.; Pérez-Camino, M.C. Valorization of a high-acidity residual oil generated in the waste cooking oils recycling industries. *Grasas y Aceites* **2019**, *40*, e335.
7. García Martín, J.F. Optical path length and wavelength selection using Vis/NIR spectroscopy for olive oil's free acidity determination. *Int. J. Food Sci. Technol.* **2015**, *50*, 1461–1467. [\[CrossRef\]](#)
8. Marquez, A.J.; Díaz, A.M.; Reguera, M.I.P. Using optical NIR sensor for on-line virgin olive oils characterization. *Sens. Actuators B Chem.* **2005**, *107*, 64–68. [\[CrossRef\]](#)
9. Lagardere, L.; Lechat, H.; Lacoste, F. Détermination de l'acidité et de l'indice de peroxyde dans les huiles d'olive vierges et dans les huiles raffinées par spectrométrie proche infrarouge à transformée de Fourier. *OCL Ol Corps Gras Lipides* **2004**, *11*, 70–75. [\[CrossRef\]](#)
10. EU Standard Methods. Commission Regulation (EEC) No 2568/91 on the characteristics of olive oil and olive-residue oil and on the relevant methods of analysis. *Off. J. Eur. Communities* **1991**, *24*, 1–15.
11. European Union. Commission implementing regulation (EU) No 1348/2013 amending Regulation (EEC) No 2568/91. *Off. J. Eur. Union* **2013**, *2013*, 31–67.
12. Shenk, J.S.; Westerhaus, M. Calibration the ISI way. In *Near Infrared Spectrosc Futur Waves*; Davies, A.M.C., Williams, P.C., Eds.; NIR Publications: Chichester, UK, 1996; pp. 198–202.
13. Shenk, J.S.; Workman, J.J.J.; Westerhaus, M.O. Application of NIR Spectroscopy to Agricultural Products. In *Handbook of Near-Infrared Analysis*; Burns, D.A., Ciurczak, E.W., Eds.; Dekker Inc.: New York, NY, USA, 2001; pp. 383–431.
14. Fearn, T. Assessing calibrations: SEP, RPD, RER and R2. *NIR News* **2002**, *13*, 12–13. [\[CrossRef\]](#)



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