

Rapid Iodine Value Estimation Using a Handheld Raman Spectrometer for On-Site, Reagent-Free Authentication of Edible Oils

Sanoop Pulassery, Bini Abraham, Nandu Ajikumar, Arun Munnilath, and Karuvath Yoosaf*



Cite This: *ACS Omega* 2022, 7, 9164–9171



Read Online

ACCESS |



Metrics & More

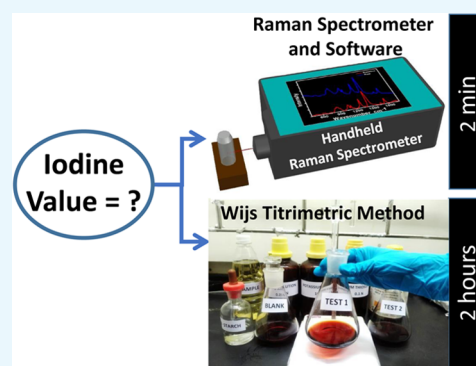


Article Recommendations



Supporting Information

ABSTRACT: Edible oil adulteration is a common and serious issue faced by human societies across the world. Iodine value (IV), the total unsaturation measure, is an authentication tool used by food safety officers and industries for edible oils. Current wet titrimetric methods (e.g., Wijs method) employed for IV estimation use dangerous chemicals and elaborate procedures for analysis. Alternate approaches for oil analysis require sophisticated and costly equipment such as gas chromatography (GC), liquid chromatography, high-performance liquid chromatography, mass spectrometry (MS), UV-Visible, and nuclear magnetic resonance spectroscopies. Mass screening of the samples from the market and industrial environment requires a greener, fast, and more robust technique and is an unmet need. Herein, we present a handheld Raman spectrometer-based methodology for fast IV estimation. We conducted a detailed Raman spectroscopic investigation of coconut oil, sunflower oil, and intentionally adulterated mixtures with a handheld device having a 785 nm excitation source. The obtained data were analyzed in conjunction with the GC–MS results and the conventional wet Wijs titrimetric estimated IVs. Based on these studies, a specific equation for IV estimation is derived from the intensity of identified Raman spectral bands. Further, an algorithm is designed to automate the signal processing and IV estimation, and a stand-alone graphical user interface is created in user-friendly LabVIEW software. The data acquisition and analysis require < 2 minutes, and the estimated statistical parameters such as the R^2 value (0.9), root-mean-square error of calibration (1.3), and root-mean-square error of prediction (0.9) indicate that the demonstrated method has a high precision level. Also, the limit of detection and the limit of quantification for IV estimation through the current approach is ~ 1 and ~ 3 gI₂/100 g oil, respectively. The IVs of different oils, including hydrogenated vegetable oils, were evaluated, and the results show an excellent correlation between the estimated and reported ones.



INTRODUCTION

Food adulteration is a worldwide problem causing a threat to public health and the economy.^{1,2} Edible oil is one of the inevitable components of the human diet and is an excellent nutritional source for tissue development. Chemically, edible oils are triglyceride mixtures of various fatty acids. The chain length, the substitution pattern, and the unsaturation degree of fatty acids and their percentages vary from oil to oil. A meager fraction of sterols, phospholipids, carotenes, vitamins, and sugars are also present in edible oils.^{3–6} In general, the fatty acid composition of an edible oil determines its physiochemical properties. Adulteration changes the composition of edible oils and will disrupt lipid metabolism and signaling networks in human bodies. This can be a potential source of cancer, cardiovascular, neurodegenerative, and metabolic disorders.^{5,7–9} The rampant adulteration instances have necessitated an in-depth chemical analysis of foods and beverages.^{3,10–12} The essential analytical parameters used for edible oil quality estimation are the iodine value (IV), saponification value (SV), peroxide value (PV), acid value (AV), hydroxyl

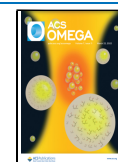
value, moisture content, and Polenske value.^{13–17} The SV and AV, respectively, provide information about the average molecular weight and the number of carboxylic acid groups of fatty acids present in the edible oil, while the IV measures the degree of unsaturation and the PV indicates its oxidative deterioration. The accurate estimation of IV is often used as an authentication tool by both the consumers and food industries and is a crucial parameter for lubricants and fuel industries.

Conventionally, a few wet chemical methods are available for the IV estimation. These include iodometry, Hübl, Wijs, Kaufmann, Rosenmund-Kuhnhehn, and acid-base titrimetric methods. Among these, the Wijs method is the most widely practiced technique, and it is also accepted internationally by

Received: September 15, 2021

Accepted: January 10, 2022

Published: March 8, 2022



most regulatory authorities like the American Oil Chemical Society (AOCS), Food Safety and Standard Authority of India (FSSAI), and so forth.^{17–19} In general, these wet titration experiments use dangerous chemicals and involve time-consuming reagent preparation and chemical analysis procedures. For example, the Wijs reagent, iodine monochloride (ICl), is a corrosive chemical and can cause skin burn, eye damage, cough, or shortness of breath. Consequently, greener and simpler approaches have been sought. The titration method developed by Shimamoto et al. uses water and a less corrosive reagent, an ethanolic solution of iodine.²⁰ Also, the procedure is faster (~15 min) and has comparable accuracy to the conventional Wijs method. Still, the titration experiments require a wet laboratory setup and are unsuitable for on-site analysis. Existing alternate approaches include modern spectroscopic and chromatographic techniques like gas chromatography (GC), liquid chromatography (LC), high-performance liquid chromatography (HPLC), mass spectrometry (MS), and ultraviolet-visible (UV-Vis), and nuclear magnetic resonance (NMR) spectroscopies.^{6,10,11,18,21,22} Most often, they are employed in combination and provide accurate and reliable results. Still, they rely on elaborate procedures and sophisticated instruments, demanding time and technical expertise. For an effective fight against adulterations, the methodologies need to be simpler, faster, and robust and must have adequate precision, aiding routine analysis in the market and industrial environment.

In this context, vibrational spectroscopies are of particular interest. They serve as fingerprint characterizing techniques and yield a wide range of information from single-shot measurements. Since the intensity of the vibrational band is directly proportional to the number of responsible molecules and functional groups, they are suitable for the composition examination of materials. Several researchers have illustrated the potential of infrared (IR) and Raman spectroscopies for the rapid characterization of edible oils and quantitative estimation of *cis*–*trans* composition and unsaturation of fatty acids present.^{23–29} At the same time, others have applied advanced spectroanalytical techniques such as multiple linear regression, genetic algorithm, principal component analysis, and partial least-squares regression for discriminating genuine samples from those adulterated and also for quantifying the extent of fraudulence.^{13,16,30–32} In particular, Raman spectroscopy is a noninvasive technique that allows rapid and nondestructive data acquisition from samples in their native state. The recent technological advancement has realized portable and handheld versions of Raman spectrometers, facilitating their on-site and industrial applications.^{33–36}

Herein, we investigate the possibility of a handheld Raman spectrometer for the rapid estimation of the IV of edible oils. The preference and type of edible oil consumption vary across the world and is largely influenced by availability, culture, different food processing traditions, and ethnicity. Table 1 lists some of the commonly used edible oils, their typical IVs, and major producers. Coconut oil (CO) is a vegetable oil having a global consumption of >3.59 million metric tons per annum.^{37,38} Though the health impact of CO was debated in the past decade, recent studies have unveiled the health benefits such as high nutritional and energy values, antiviral, antibacterial, antiprotozoal, and antioxidant properties. For example, lauric acid is a major component (~50%) in CO. Monolaurin produced from lauric acid can destroy lipid-coated viruses such as human immunodeficiency virus, herpes, and

Table 1. List of a Few Common Edible Oils, Their IVs, and Major Producers

Sl no.	oil	IV (gI ₂ /100 g oil) ^a	major producers ^b
1	coconut	6–11	Asia, Africa, Latin America, Pacific regions
2	gingelly	103–120	Tanzania, Myanmar, India
3	olive	75–94	Spain, Italy, Greece, Tunisia, Turkey, Morocco, Portugal, Syria and Algeria
4	palm	50–56	Indonesia, Malaysia
5	rice bran	90–115	India, Japan, China, Korea, Taiwan, Thailand, and Indonesia
6	sunflower	118–141	Ukraine, Russia, North America, South America
7	butter	25–42	India, European Union, USA
8	vanaspati	37–47	South Asia

^aSource: FDA Thailand⁴³ and Codex Alimentarius.⁴⁴ ^bFood and Agriculture Organization Statistical Databases (FAOSTAT)⁴⁵ and United States Department of Agriculture (USDA).⁴⁶

influenza in the human body. Trace amounts of a few identified phenolic acids in CO, such as vanillic, caffeic, ferulic, *p*-coumaric acids, and so forth, contribute to the antioxidant activity. Studies also show that consumption of CO reduces the risk of cardiovascular and Alzheimer's diseases.^{3,39–42} Due to these established health benefits, recent years have witnessed an increased demand for CO. In addition to its use in cuisines, it is also being used to produce personal care cosmetics, detergents, and biodiesel. Presently, the incidence of CO adulteration is alarmingly increasing, and they are done mainly for economic benefits. From Table 1, it is clear that CO has one of the lowest IV. In comparison, sunflower oil (SO) is reported to have the highest IV. Therefore, it is expected that a combination of these two oils permits to have a broader range of IVs. Based on this assumption, Raman spectral studies of a model system, CO adulterated with SO, were conducted using a handheld Raman spectrometer with a 785 nm excitation laser. The obtained data were analyzed in conjunction with the GC–MS results and the conventional Wijs method-estimated IV. This helped to derive a specific relation between the intensity ratios of identified Raman spectral bands and the IV of CO. Further, an algorithm is designed to automate the signal processing and IV estimation, and a stand-alone graphical user interface (GUI) is created in LabVIEW software. The entire data acquisition and analysis process take < 2 minutes, and the demonstrated method has reasonably high accuracy and precision levels. The developed method is then used to predict the IV of different oils, including hydrogenated vegetable oils, and has proven to be a successful tool for IV estimation.

MATERIALS AND METHODS

Materials. Coconut oil, sunflower oil, butter, vanaspati, castor oil, gingelly oil, palm oil, paraffin oil, olive oil, and rice bran oil were purchased from local grocery stores. 1 M ICl in acetic acid, soluble starch, and methanol (HPLC grade) were purchased from Ms. SpectroChem Pvt. Ltd, India. Carbon tetrachloride, sulfuric acid, potassium iodide (KI) (>99%), potassium dichromate (>99.5%), glacial acetic acid (100%), and sodium thiosulfate (Na₂S₂O₃, >98.0%) were purchased from Ms. Sigma Aldrich Chemicals Pvt. Ltd. Hexane was purchased from SDFCL, India.

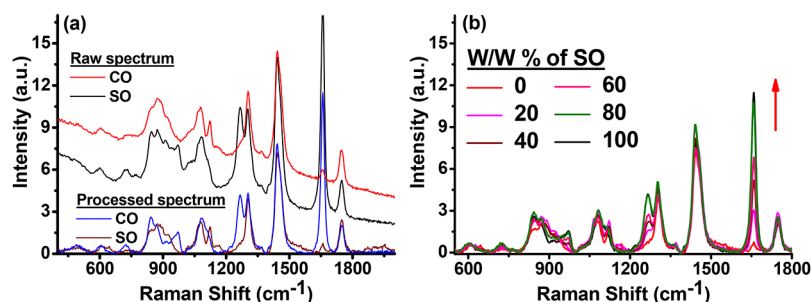


Figure 2. Raman spectra of (a) CO and SO and (b) mixtures of varying compositions. Measurement parameters: $\lambda_{\text{exc}} = 785$ nm, laser power = 37 mW, integration time = 5 s, and no. of averages = 1. The red arrow indicates the direction of peak intensity variation at 1658 cm^{-1} with the percentage composition of SO in the mixture.

carotenes, and added coloring agents. This poses a significant challenge to quantitative analysis using Raman spectroscopy. Several spectral processing tools are described in the literature, and we found that SCARF⁴⁹ is good enough for automated in-line background removal without losing much spectral information. The background-subtracted Raman spectra are presented in Figure 2a, and the significant peaks, their vibrational assignment, and relative intensities are tabulated in Table 2. The following observations can be derived from a

Table 2. Observed Raman Spectral Peaks for CO and SO and Their Vibrational Assignments^{25,50}

Raman peak (cm^{-1})	intensity (counts)		vibrational assignment
	CO	SO	
1750	2413	2017	C=O symmetric stretching
1658	699	11478	Cis RCH=CHR stretching
1442	7181	7842	CH ₂ bending (scissoring)
1300	3933	4330	CH ₂ bending (twisting)
1265	728	4195	Cis RCH=CHR bending (scissoring)
1125	1914	987	C–C aliphatic in-phase bending
1080	2263	2537	–CH ₃ bending
968		1554	trans RCH=CHR bending
860	2123	2617	C–C stretching

close analysis of these data. The Raman spectra of CO and SO exhibited identical bands at the same frequencies. However, the notable difference was mainly in their relative intensities.

For example, the peak at 1658 cm^{-1} , due to C=C stretching vibrations, is the strongest for SO and is at least one order of magnitude less intense for CO. This could be understood from the fact that SO is highly unsaturated, and hence the peak corresponding to C=C stretching vibrations gets the highest intensity. The highest intensity peaks for CO appeared at 1442 and 1300 cm^{-1} , corresponding to CH₂ bending modes. Also, the band at 1262 cm^{-1} assigned to cis RCH=CHR, that is, =C–H bending (scissoring), is negligible in the case of CO when compared with SO. Figures 2b and S2 (Supporting Information) represent the observed Raman spectra of CO/SO mixtures of varying compositions. As expected, a steady rise in the peak intensities at 971 , 1265 , and 1658 cm^{-1} is evident as the percentage of SO in the mixture increases. This is because the main components of SO are unsaturated linoleic acid and oleic acid, and the mentioned Raman spectral bands are contributed by C=C stretching and bending modes.

IV from Raman Spectral Measurements. From the linear graph depicted in Figure 1a, the relation between the Wijs method-measured IV and w/w % composition of SO in the mixture can be represented by eq 2

$$\text{iodine value, IV} = m_1 \left(\frac{W}{W} \right)_{\text{SO}} + C_1 \quad (2)$$

where the slope, m_1 , is the rate of change of IV with the percentage variation of SO in the mixture. The y-intercept, C_1 , is the IV of pure CO. The linear fitting of the plot returned an R^2 value of 0.999 (Figure 1a), and the extracted values of m_1 and C_1 are, respectively, 1.208 and 7.672.

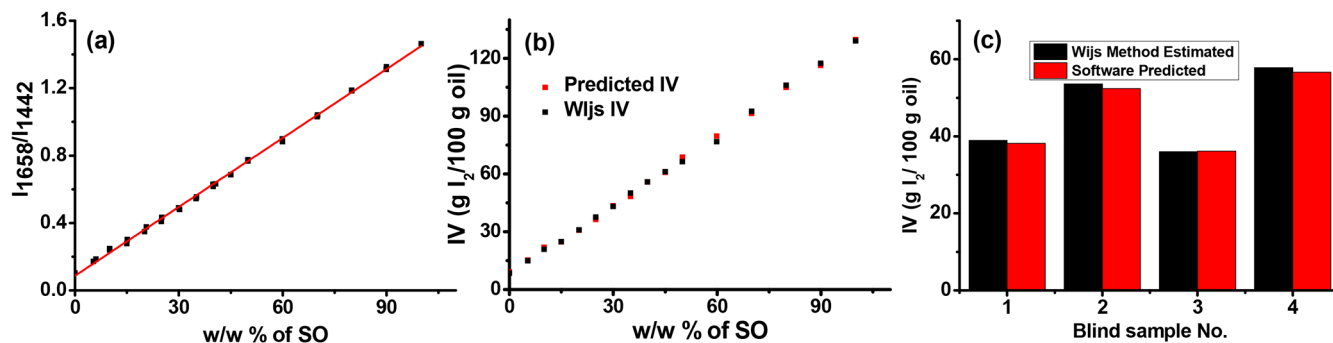


Figure 3. Plot showing the (a) variation of the peak ratio against the weight percentage of SO in the mixture, (b) comparison of IVs estimated through the Wijs method and software at different known compositions of SO in CO, and (c) comparison of the values estimated through Wijs method and software for blind samples.

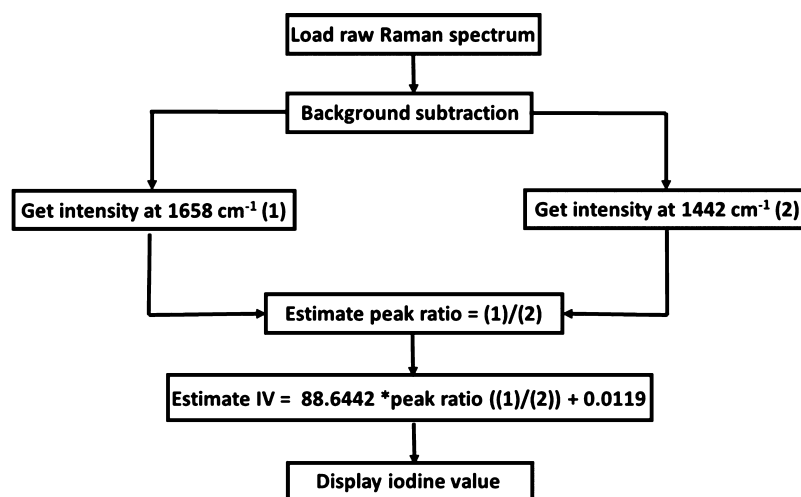


Figure 4. Algorithm for the estimation of IV.

A few previous studies have illustrated that the intensity ratio of peaks corresponding to C=C and CH₂ can be used to measure the unsaturation degree in oils and lipids in biological samples.^{25,51} In the current work, these peaks appeared at 1658 and 1442 cm⁻¹. Hence, we studied the variation of peak ratio of these bands as a function of the percentage composition of SO in the mixture (Figure 3a). The obtained linear plot is best fitted with eq 3

$$\text{peak ratio, } \frac{I_{1658}}{I_{1442}} = m_2 \left(\frac{W}{W} \% \right)_{\text{SO}} + C_2 \quad (3)$$

Slope, m_2 , corresponds to the rate of change of peak ratio against the percentage composition of SO in the mixture. The y-intercept, C_2 , is the peak ratio of pure CO. The linear fit of Figure 3a yielded an R^2 value of 0.999, and the estimated values of m_2 and C_2 , respectively, are 0.01363 and 0.0864. From eqs 2 and 3, the equation for calculating the IV from the peak ratio can be deduced as

$$\text{iodine value, IV} = m_3 \frac{I_{1658}}{I_{1442}} + C_3 \quad (4)$$

where

$$m_3 = \frac{m_1}{m_2} \quad (5)$$

and

$$C_3 = C_1 - \frac{m_1}{m_2} C_2 \quad (6)$$

From eqs 5 and 6, slope m_3 and intercept C_3 are calculated as 88.644 and 0.012, respectively.

Algorithm for the Estimation of IV. Knowing the relationship between the IV and the peak intensity ratio and the values of m_3 and C_3 , we designed a stand-alone GUI to automate the signal processing and IV estimation. The data flow involved in the algorithm is presented in Figure 4 and is described as follows. In the first step, the raw spectrum (csv format) recorded using a handheld Raman spectrometer is loaded into the IV estimator. Subsequently, the data undergo automated background subtraction through the SCARF method with a set of fixed values such as third-order polynomial, rolling circle filter radius (rcf) as 60, zero baseline,

and Savitzky–Golay filtering side points as 60. In the consecutive steps, the software measures the intensities at 1658 and 1442 cm⁻¹. The estimated ratio of these intensity values is fed to the equation of the form (4), and finally, the calculated IV is displayed. The whole process takes place within a few seconds.

To test the accuracy and reliability of the method, we analyzed the statistical error parameters such as the R^2 value, mean percentage error (MPE), and root-mean-square error of calibration and prediction (RMSEC and RMSEP) for both known and blind samples (Figure 5 and Table S4, Supporting

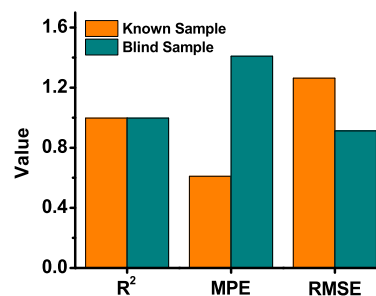


Figure 5. Plot showing the comparison of statistical error parameters for the calibration and validation of the IV estimator software.

Information). Figure 3b and 3c represent the comparison of predicted versus Wijs method estimated IVs. The IV versus composition returned a linear plot with R^2 values (0.9) for known samples, indicating higher linearity and correlation between software predicted IVs and those from the Wijs titrimetric method.

The relative error calculated for calibration and blind samples varied from -0.07 to 0.04 (Tables S3, S5 and Figure S3, Supporting Information). MPE is the measure of the precision of the experimental value to the predicted one. The obtained values are 0.6% and 1.4% for known and blind samples, respectively, suggesting good agreement between IVs obtained from the developed GUI and the Wijs method of titration. RMSEC and RMSEP are the square roots of the average of squared differences between IVs predicted by software and the Wijs method for calibration and blind samples, respectively. Generally, a lower value of RMSE infers a classic match between the predicted and observed values of

measurement. In the present case, RMSEC and RMSEP are 1.3 and 0.9, respectively, indicating the excellent performance of the developed method.

Listed in Tables S6–S11 of the [Supporting Information](#) are the results of some of the matrix effects investigated. In general, it is observed that experimental parameters, such as the type of sample container, the environment of measurements, and the presence of other chemicals, and instrumental parameters such as laser power, integration time, and the number of accumulations have a negligible effect on the determined IV.⁵² For the quantitative evaluation of the intra/interday precisions and accuracies, IVs of five different compositions (0, 25, 50, 75, and 100% w/w SO in CO) were estimated through both Wijs and developed methods at four different time intervals ([Table S12](#), [Supporting Information](#)). For a particular composition and method, the IVs estimated at different time intervals varied by a maximum of ± 0.5 . However, the relative standard deviation percentage showed a value of 6.4% for the samples with low IVs (pure COs) and underwent a continuous decrease with an increase in the IV (i.e., the percentage composition of SO in the sample). Similarly, the observed *t*-critical value is 2.4 ($n_1 = n_2 = 4$, $\alpha = 0.05$), which suggested that statistically equivalent results were obtained between the IVs estimated from both methods ($t_{\text{calculated}} > t_{\text{critical}}$) and is an indication of more than 95% of confidence level ([Table S12](#)). The limit of detection (LoD) and limit of quantification (LoQ) were, respectively, estimated using the formula $3\sigma/m$ and $10\sigma/m$, where σ is the standard deviation and m is the slope of the residual linear regression plot ([Figure S4](#), [Supporting Information](#)). For the currently developed method, LoD and LoQ are estimated to be ~ 1 gI₂/100 g oil and ~ 3 gI₂/100 g oil, respectively.^{53,54}

To evaluate the wider applicability of the developed method further, 10 different oils were analyzed, including hydrogenated vegetable oils. Reported in [Figure S5](#) ([Supporting Information](#)) are the Raman spectra of these oils, and [Table S13](#) ([Supporting Information](#)) shows the comparison of the estimated IVs along with literature reported values. It is found that for the samples investigated, the IVs calculated from the Raman spectrum fall well within the range of literature-reported values. [Table S14](#) ([Supporting Information](#)) lists the comparison of the cost and easiness of the current method against some of the presently available techniques. As stated before, techniques like NMR and GC–MS provide accurate results, but the instruments are highly sophisticated and require trained technicians to operate. The titrimetric methods involve the use of wet chemical laboratory, corrosive chemicals, and sample preparation procedures. UV–vis spectroscopy requires reaction with certain chemicals. The IR and NIR instruments require specific sample containers and a closed chamber. On the contrary, as illustrated in [Table S15](#) ([Supporting Information](#)), Raman spectroscopy allows direct measurements using simple glass containers and works even in an open environment ([Figure S6](#), [Supporting Information](#)).

CONCLUSIONS

Herein, we demonstrated a simple, reagent-free, and rapid method to determine the IV of edible oil. The judicious analysis of Raman spectra with GC–MS and the Wijs method-estimated IV helped us correlate unsaturation with spectral information. A specific relation is derived to estimate the IV of the oils using the peak ratio of contributions from unsaturation (1658 cm^{-1}) to saturation (1442 cm^{-1}). The incorporation of

SCARF helped us automate the process of background subtraction and IV estimation. The estimated statistical error parameters for blind samples such as the R^2 value (0.9), MPE ($0.6_{\text{known}}, 1.4_{\text{blind}}$), RMSEC (1.3), and RMSEP (0.9) indicate the high precision of the developed technique. The paired-*t* test estimated for sample compositions located in the low, medium, and high concentration levels of the calibration graph indicated more than 95% of confidence level. Also, the current method has got reasonably good LoD (~ 1 gI₂/100 g oil) and LoQ (~ 3 gI₂/100 g oil) for the estimation IVs. Compared to other presently available techniques, the present method is completely reagent-free, and the measurements can be performed using simple glass vials or in their native state. Yet, another attraction of the method is that the analysis is performed using a handheld Raman spectrometer, and the developed software module enables even a layperson to perform the analysis. Similar approaches can be developed to estimate other quality parameters such as peroxide and acid values of edible oils. We believe that the work described herein can elevate the use of Raman spectroscopy for fast quality analysis and authentication of edible oils from the market and industrial environment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c05123>.

GC–MS measurement conditions, chromatogram, estimated chemical composition, Raman spectra of different oils and CO/SO mixtures, comparison of IV estimated through Wijs and Raman spectral method, equations and results of statistical error parameters, matrix effects, calibration graph used for LoD and LoQ estimation, validation results with various oils, cost and convenience comparison with other presently available methods, and pictorial representation of data acquisition using a handheld Raman spectrometer ([PDF](#))

AUTHOR INFORMATION

Corresponding Author

Karuvath Yoosaf – *Photosciences and Photonics Section, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram 695019 Kerala, India; Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India; Research Centre, University of Kerala, Thiruvananthapuram 695034 Kerala, India; orcid.org/0000-0002-8837-4490; Phone: 0091-471-2515477; Email: yoosafk@niist.res.in*

Authors

Sanoop Pulassery – *Photosciences and Photonics Section, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram 695019 Kerala, India; Research Centre, University of Kerala, Thiruvananthapuram 695034 Kerala, India; orcid.org/0000-0003-1836-9618*

Bini Abraham – *Photosciences and Photonics Section, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram 695019 Kerala, India; Academy of*

Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India; orcid.org/0000-0002-1694-4204

Nandu Ajikumar – Photosciences and Photonics Section, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram 695019 Kerala, India; Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India; orcid.org/0000-0001-8394-0476

Arun Munnalath – Photosciences and Photonics Section, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram 695019 Kerala, India; orcid.org/0000-0002-5832-9920

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsomega.1c05123>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Sanoop Pulassery received research fellowship from the Kerala State Council for Science, Technology and Environment (KSCSTE), Government of Kerala, India, grant no. 001/FSHP-MAIN/2017/KSCSTE. The authors (Karuvath Yoosaf and Bini Abrham) received research funding from the Department of Biotechnology, Ministry of Science and Technology, India, grant no. BT/PR22475/NNT/28/1193/2016. Council for Scientific and Industrial Research, Ministry of Science and Technology, India also supported this research through Mission mode HCP0031 and Fast Track Translation grant MLP0039. This manuscript is contribution no. NIIST/2021/Aug/261 from the CSIR-National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram.

REFERENCES

- (1) Robson, K.; Dean, M.; Haughey, S.; Elliott, C. A comprehensive review of food fraud terminologies and food fraud mitigation guides. *Food Control* **2021**, *120*, 107516.
- (2) Gizaw, Z. Public health risks related to food safety issues in the food market: a systematic literature review. *Environ. Health Prev. Med.* **2019**, *24*, 68.
- (3) Tena, N.; Wang, S. C.; Aparicio-Ruiz, R.; García-González, D. L.; Aparicio, R. In-Depth Assessment of Analytical Methods for Olive Oil Purity, Safety, and Quality Characterization. *J. Agric. Food Chem.* **2015**, *63*, 4509–4526.
- (4) Çelik, S. E.; Asfoor, A.; Şenol, O.; Apak, R. Screening Method for Argan Oil Adulteration with Vegetable Oils: An Online HPLC Assay with Postcolumn Detection Utilizing Chemometric Multidata Analysis. *J. Agric. Food Chem.* **2019**, *67*, 8279–8289.
- (5) Zhou, Y.; Zhao, W.; Lai, Y.; Zhang, B.; Zhang, D. Edible Plant Oil: Global Status, Health Issues, and Perspectives. *Front. Plant Sci.* **2020**, *11*, 1315.
- (6) Zhang, L.; Li, P.; Sun, X.; Wang, X.; Xu, B.; Wang, X.; Ma, F.; Zhang, Q.; Ding, X. Classification and Adulteration Detection of Vegetable Oils Based on Fatty Acid Profiles. *J. Agric. Food Chem.* **2014**, *62*, 8745–8751.
- (7) Mishra, V.; Mishra, M.; Ansari, K. M.; Chaudhari, B. P.; Khanna, R.; Das, M. Edible oil adulterants, argemone oil and butter yellow, as aetiological factors for gall bladder cancer. *Eur. J. Cancer* **2012**, *48*, 2075–2085.
- (8) Bester, D.; Esterhuysen, A. J.; Truter, E. J.; van Rooyen, J. Cardiovascular effects of edible oils: a comparison between four popular edible oils. *Nutr. Res. Rev.* **2010**, *23*, 334–348.
- (9) Anton, S. D.; Heekin, K.; Simkins, C.; Acosta, A. Differential effects of adulterated versus unadulterated forms of linoleic acid on cardiovascular health. *J. Integr. Med.* **2013**, *11*, 2–10.
- (10) Salah, W. A.; Nofal, M. Review of some adulteration detection techniques of edible oils. *J. Sci. Food Agric.* **2021**, *101*, 811–819.
- (11) Yadav, S. Edible oil adulterations: Current issues, detection techniques, and health hazards. *Int. J. Chem. Stud.* **2018**, *6*, 1393–1397.
- (12) Meenu, M.; Cai, Q.; Xu, B. A critical review on analytical techniques to detect adulteration of extra virgin olive oil. *Trends Food Sci. Technol.* **2019**, *91*, 391–408.
- (13) Xu, L.; Zhu, X.; Yu, X.; Huan, Z.; Wang, X. Rapid and Simultaneous Determination of the Iodine Value and Saponification Number of Edible Oils by FTIR Spectroscopy. *Eur. J. Lipid Sci. Technol.* **2018**, *120*, 1700396.
- (14) Jiang, X.; Li, S.; Xiang, G.; Li, Q.; Fan, L.; He, L.; Gu, K. Determination of the acid values of edible oils via FTIR spectroscopy based on the OH stretching band. *Food Chem.* **2016**, *212*, 585–589.
- (15) Rohman, A. Infrared spectroscopy for quantitative analysis and oil parameters of olive oil and virgin coconut oil: A review. *Int. J. Food Prop.* **2017**, *20*, 1447–1456.
- (16) Seweh, E. A.; Xiaobo, Z.; Tao, F.; Jiachen, S.; Tahir, H. E.; Arslan, M. Multivariate analysis of three chemometric algorithms on rapid prediction of some important quality parameters of crude shea butter using Fourier transform-near infrared spectroscopy. *J. Near Infrared Spectrosc.* **2019**, *27*, 220–231.
- (17) McCutcheon, J. W. Wijs Iodine Method. *Ind. Eng. Chem., Anal. Ed.* **1940**, *12*, 465.
- (18) Kyriakidis, N. B.; Katsiloulis, T. Calculation of iodine value from measurements of fatty acid methyl esters of some oils: Comparison with the relevant American Oil Chemists Society method. *J. Am. Oil Chem. Soc.* **2000**, *77*, 1235–1238.
- (19) Firestone, D. Determination of the Iodine Value of Oils and Fats: Summary of Collaborative Study. *J. AOAC Int.* **1994**, *77*, 674–676.
- (20) Shimamoto, G. G.; Aricetti, J. A.; Tubino, M. A Simple, Fast, and Green Titrimetric Method for the Determination of the Iodine Value of Vegetable Oils Without Wijs Solution (ICI). *Food Anal. Methods* **2016**, *9*, 2479–2483.
- (21) Miyake, Y.; Yokomizo, K.; Matsuzaki, N. Rapid determination of iodine value by ¹H nuclear magnetic resonance spectroscopy. *J. Am. Oil Chem. Soc.* **1998**, *75*, 15–19.
- (22) Haryati, T.; Che Man, Y. B.; Ghazali, H. M.; Asbi, B. A.; Buana, L. Determination of iodine value of palm oil based on triglyceride composition. *J. Am. Oil Chem. Soc.* **1998**, *75*, 789–792.
- (23) An, Z.; Jiang, X.; Xiang, G.; Fan, L.; He, L.; Zhao, W. A simple and practical method for determining iodine values of oils and fats by the FTIR spectrometer with an infrared quartz cuvette. *Anal. Methods* **2017**, *9*, 3669–3674.
- (24) Bailey, G. F.; Horvat, R. J. Raman spectroscopic analysis of the cis/trans isomer composition of edible vegetable oils. *J. Am. Oil Chem. Soc.* **1972**, *49*, 494–498.
- (25) Dymińska, L.; Calik, M.; Albeggar, A. M. M.; Zając, A.; Kostyń, K.; Lorenc, J.; Hanuza, J. Quantitative determination of the iodine values of unsaturated plant oils using infrared and Raman spectroscopy methods. *Int. J. Food Prop.* **2017**, *20*, 2003–2015.
- (26) Sedman, J.; van de Voort, F. R.; Ismail, A. A.; Maes, P. Industrial validation of fourier transform infrared trans and iodine value analyses of fats and oils. *J. Am. Oil Chem. Soc.* **1998**, *75*, 33–39.
- (27) Wang, P.; Sun, J.; Zhang, T.; Liu, W. Vibrational spectroscopic approaches for the quality evaluation and authentication of virgin olive oil. *Appl. Spectrosc. Rev.* **2016**, *51*, 763–790.
- (28) Jiménez-Sanchidrián, C.; Ruiz, J. R. Use of Raman spectroscopy for analyzing edible vegetable oils. *Appl. Spectrosc. Rev.* **2016**, *51*, 417–430.
- (29) Gooch, E. E. Determination of the Iodine Value of Selected Oils: An Experiment Combining FTIR Spectroscopy with Iodometric Titrations. *J. Chem. Educ.* **2001**, *6*, 7–9.

- (30) van de Voort, F. R.; Sedman, J.; Emo, G.; Ismail, A. A. Rapid and direct iodine value and saponification number determination of fats and oils by attenuated total reflectance/fourier transform infrared spectroscopy. *J. Am. Oil Chem. Soc.* **1992**, *69*, 1118–1123.
- (31) Jiménez-Carvelo, A. M.; González-Casado, A.; Bagur-González, M. G.; Cuadros-Rodríguez, L. Alternative data mining/machine learning methods for the analytical evaluation of food quality and authenticity – A review. *Int. Food Res. J.* **2019**, *122*, 25–39.
- (32) Lim, K.; Pan, K.; Yu, Z.; Xiao, R. H. Pattern recognition based on machine learning identifies oil adulteration and edible oil mixtures. *Nat. Commun.* **2020**, *11*, 5353.
- (33) Lebanov, L.; Paull, B. Smartphone-based handheld Raman spectrometer and machine learning for essential oil quality evaluation. *Anal. Methods* **2021**, *13*, 4055–4062.
- (34) Ellis, D. I.; Muhamadali, H.; Xu, Y.; Eccles, R.; Goodall, I.; Goodacre, R. Rapid through-container detection of fake spirits and methanol quantification with handheld Raman spectroscopy. *Analyst* **2019**, *144*, 324–330.
- (35) Rodríguez-Saona, L.; Aykas, D. P.; Borba, K. R.; Urtubia, A. Miniaturization of optical sensors and their potential for high-throughput screening of foods. *Curr. Opin. Food Sci.* **2020**, *31*, 136–150.
- (36) Emmanuel, N.; Nair, R. B.; Abraham, B.; Yoosaf, K. Fabricating a Low-Cost Raman Spectrometer to Introduce Students to Spectroscopy Basics and Applied Instrument Design. *J. Chem. Educ.* **2021**, *98*, 2109–2116.
- (37) Apraku, A.; Liu, L.; Ayisi, C. L. Trends and Status of Dietary Coconut Oil in Aquaculture Feeds. *Rev. Fish. Sci. Aquacult.* **2017**, *25*, 126–132.
- (38) Pham, L. J. Coconut (*Cocos nucifera*). In *Industrial Oil Crops*; McKeon, T. A., Hayes, D. G., Hildebrand, D. F., Weselake, R. J., Eds.; AOCS Press, 2016, pp 231–242.
- (39) Hewlings, S. Coconuts and Health: Different Chain Lengths of Saturated Fats Require Different Consideration. *J. Cardiovasc. Dev. Dis.* **2020**, *7*, 59.
- (40) Ma, Z. F.; Lee, Y. Y. Virgin Coconut Oil and its Cardiovascular Health Benefits. *Nat. Prod. Commun.* **2016**, *11*, 1151.
- (41) Babu, A. S.; Veluswamy, S. K.; Arena, R.; Guazzi, M.; Lavie, C. J. Virgin Coconut Oil and Its Potential Cardioprotective Effects. *Postgrad. Med.* **2014**, *126*, 76–83.
- (42) Deen, A.; Visvanathan, R.; Wickramarachchi, D.; Marikkar, N.; Nammi, S.; Jayawardana, B. C.; Liyanage, R. Chemical composition and health benefits of coconut oil: an overview. *J. Sci. Food Agric.* **2021**, *101*, 2182–2193.
- (43) http://food.fda.moph.go.th/law/data/announ_moph/V.English/P421_E.pdf (accessed on Dec 28, 2021).
- (44) <https://www.fao.org/fao-who-codexalimentarius/codex-texts/list-standards/en/> (accessed on Dec 28, 2021).
- (45) <http://faostat.fao.org/> (accessed on Dec 28, 2021).
- (46) <https://www.fas.usda.gov/data/oilseeds-world-markets-and-trade> (accessed on Dec 28, 2021).
- (47) Ehimen, E. A.; Sun, Z. F.; Carrington, C. G. Variables affecting the in situ transesterification of microalgae lipids. *Fuel* **2010**, *89*, 677–684.
- (48) Bernert, J. T., Jr. Gas Chromatography and Lipids, a Practical Guide. William W. Christie. Ayr, Scotland: The Oily Press. 307 pp, \$52.50, ISBN 0-9514171-X. *Clin. Chem.* **1989**, *35*, 2021.
- (49) James, T. M.; Schlösser, M.; Lewis, R. J.; Fischer, S.; Bornschein, B.; Telle, H. H. Automated Quantitative Spectroscopic Analysis Combining Background Subtraction, Cosmic Ray Removal, and Peak Fitting. *Appl. Spectrosc.* **2013**, *67*, 949–959.
- (50) De Géa Neves, M.; Poppi, R. J. Monitoring of Adulteration and Purity in Coconut Oil Using Raman Spectroscopy and Multivariate Curve Resolution. *Food Anal. Methods* **2018**, *11*, 1897–1905.
- (51) Samek, O.; Jonáš, A.; Pilát, Z.; Zemánek, P.; Nedbal, L.; Triska, J.; Kotas, P.; Trtílek, M. Raman Microspectroscopy of Individual Algal Cells: Sensing Unsaturation of Storage Lipids in vivo. *Sensors* **2010**, *10*, 8635–8651.
- (52) Afseth, N. K.; Wold, J. P.; Segtnan, V. H. The potential of Raman spectroscopy for characterisation of the fatty acid unsaturation of salmon. *Anal. Chim. Acta* **2006**, *572*, 85–92.
- (53) Shrivastava, A.; Gupta, V. Methods for the determination of limit of detection and limit of quantitation of the analytical methods. *Chron. Young Sci.* **2011**, *2*, 21–25.
- (54) Sajitha, M.; Abraham, B.; Nelliyl, R. B.; Yoosaf, K. Chemically Etched Nanoporous Copper and Galvanically Displaced Silver Nanoflowers for SERS Sensing. *ACS Appl. Nano Mater.* **2021**, *4*, 10038–10046.

Recommended by ACS

Study of Ultrahigh-Performance Liquid Chromatography Electrospray Ionization Q-Orbitrap Mass Spectrometry and Various Extraction Methods for Fingerprinting and Identi...

Jian Wang and Willis Chow

JULY 13, 2022

ACS FOOD SCIENCE & TECHNOLOGY

READ 

Compositional Analysis of High-TAN Sudanese Crude Oil Using High-Resolution Mass Spectrometry and Study of the Effect of Temperature and Catalyst on Acidic Composition

Haifa Shamseldin Mohamed Salim, Mustafa Abbas Mustafa, et al.

MAY 13, 2022

ACS OMEGA

READ 

Improved Quantification by Nuclear Magnetic Resonance Spectroscopy of the Fatty Acid Ester Composition of Extra Virgin Olive Oils

Gabriel Rossetto, Mathias Nilsson, et al.

JULY 11, 2022

ACS FOOD SCIENCE & TECHNOLOGY

READ 

Investigation of the Impact of a Pesticide Adjuvant on Dimethoate Persistence, Penetration, and Stability on Apples Using Surface-Enhanced Raman Spectroscopy

Danhui Wang, Lili He, et al.

JUNE 27, 2022

ACS AGRICULTURAL SCIENCE & TECHNOLOGY

READ 

Get More Suggestions >