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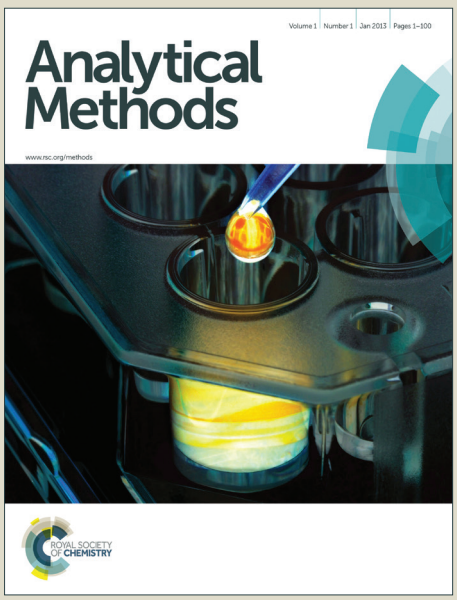

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ARTICLE

Qualitative Analysis of Edible Oil Oxidation by FTIR Spectroscopy Using Mesh "Cell"

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To develop a feasible, green, and fast qualitative detection method for identifying edible oil oxidation, peroxide and acid values of oils were measured according to the American Oil Chemists' Society standard. A reference set was developed using common edible oils as raw materials. The qualitative discrimination between oxidised and non-oxidised oils was calibrated based on Fourier transform infrared (FTIR) procedures, which used a mesh cell as spectral acquisition accessory and combined with Mahalanobis analysis. At the wave number range from 3750 cm^{-1} to 3150 cm^{-1} after oil film path length normalisation, the recognition rates of the calibration and the external validation models reached up to 100% and 96.9% respectively. The results therefore indicated the method as effective as standard methods and others in predicting edible oil oxidation. In conclusion, applying mesh cell-based FTIR method to qualitatively analyse edible oil oxidation is feasible.

Introduction

The oxidation of fats and oils is an important deteriorative reaction which has significant commercial implications on the products in terms of their value. The initial oxidation products that accumulate in triacylglycerols are hydroperoxides, which may subsequently break down to form lower-molecular weight compounds, such as alcohols, aldehydes, free fatty acids and ketones, and thereby, ultimately leads to a rancid product.[1] Thus, the oxidation level of oil and fat is an important quality criterion for the food industry. Oxidation of oils is not desired not only because it produces rancid flavours, but also because of its negative effect on the nutritional quality and safety of a product. The formation of oxidation products may also be harmful to the human bodies and lead to health concerns.[2–4]

The American Oil Chemists' Society (AOCS) has a number of official methods to determine the oxidative status of oil, and the most common ones are to measure peroxide and acid values (PV and AV, respectively). The conventional AOCS method used to determine PV involves iodometric titration which measures the iodine liberated from potassium iodide after reacting with the peroxides present in oil samples.[5,6,7] To determine AV, one has to calculate the milligrams of KOH required to neutralise the free fatty acids (FFAs) in 1 g of sample according to the AOCS

official method.[8] To express FFA content as oleic acid percentage, the AV can be divided by 1.99.[9] These chemical methods are not difficult to perform, however, they are time consuming, destructive to the samples, costly and they require large quantity of glassware, samples and potentially hazardous reagents. [10]

To counter the drawbacks of the official methods, a number of new spectroscopic methods to measure lipid oxidation have been developed over the past few years.[10,11] Fourier transform infrared (FTIR) technique is a powerful tool for analysing edible oils, both qualitatively and quantitatively, and it has been used to monitor oil oxidation.[12–15] There are limitations with FTIR and researchers have investigated in various techniques for overcoming the limitations. However, these newly developed techniques still have their defects. The attenuated total reflection (ATR) approach is impractical because of its short path length cell and weak signal, thus, ATR has low accuracy.[16] Van de Voort and colleagues have worked toward developing instrumental methods for the quantitative analysis of edible oils based on FTIR spectroscopy.[17,18] Initially, they used a chemometric approach based on the measurement of the characteristic O–H stretching absorption band of hydroperoxides at 3444 cm^{-1}.[17] Subsequently, they developed a much simpler and more accurate method involving the use of the well-characterised stoichiometric reaction of triphenylphosphine with hydroperoxides to form triphenylphosphine oxide.[19] However, the sample handling difficulties associated with the mid-infrared (IR) analysis of neat oils in the transmission mode limited its practical application.[18,20] To overcome the handling difficulty of the viscous oil samples, Ma et al. investigated the quantification of hydroperoxides by using disposable polyethylene IR cards (e.g., 3M IR cards (Pike Technologies, Madison, WI ,USA)) on edible oils. [19,21] The procedure was simple, but the sensitivity was low, and the effective path length was vulnerable to disturbance. Spectral reconstitution (SR) was another technique investigated, and it was applied to simplify and automate the FTIR method to determine the PV of edible oil.[22] This technique also used the SR procedure to eliminate cell loading problems.[23] However, in the SR method, viscous oil samples loaded into narrow flow-transmission cells made the cells difficult to clean, and thus, led to a time consuming process. Moreover, the easy cross-contamination of the cells can make the procedure less accurate and not desirable.[24]

Russin et al. used disposable polytetrafluoroethylene polymer IR (PIR) cards as accessory to oxidise the edible oils rapidly and to simultaneously monitor the extent of oxidation at moderate temperature (58°C) by FTIR spectroscopy.This method is advantageous because it's simple, rapid, and real-time monitoring. However, the method had poor temperature adaptability and the PIR cards could not be used repeatedly.[15,25] Currently, oil analysis commonly involves the use of 3M series IR card made by 3M manufacturers (Pike Technologies, Madison, WI, USA) and FTIR-PIR cards produced by Thermo-Nicolet (Thermo Scientific, Inc.). These cards are all expensive and the high price of such cards limits their practical applications. Garcia-Gonza et al. used a reusable stainless steel mesh "cell" as a novel IR sample handling accessory to monitor and study the oxidation processes of edible oils under moderate temperature.[26] They found that mesh cell can be used for real-time monitoring of lipid oxidation process because of its high thermoresistance and better functionality under infrared light, which promoted the quality and reproducibility of spectra. [26]

The stainless steel mesh cell is reusable during the test and has less impact on accuracy. It was an environmentally friendly, simple and efficient method, which could be useful in comparing the relative performance of antioxidants, as well as evaluating the oxidative stability of oils, among other applications. Recently, our research group has developed a new technique for spectral acquisition using polyethylene (PE) film.[27,28] In the PE procedure, the spectra of the oil films were collected by using a PE film background spectrum. The path length of oil films was determined by a CH combination band calibration and was normalised to a fixed path length of 0.15 mm. This method can be applied easily, and it is free from difficulties associated with the viscosity of oils, which is practical and easy to operate.

In the present study, different kinds of common edible oils were collected, and their characteristic spectra were measured using FTIR technique. A reusable stainless steel mesh cell was used as a test accessory after different oxidation processes based on the same principle. A new model for qualitative identification of edible oil oxidation was developed and validated. The performance of the model was evaluated by analyzing test samples and comparing the prediction to the true oxidation status as determined using AOCS official methods. The new mesh cell-based FTIR method achieved rapid detection of qualitative analysis of common edible oils oxidation, which can provide a practical reference for the rapid determination of the degree of oxidation in edible oils.

Material and methods

Materials and reagents

A variety of edible oils (olive, peanut, soybean, pepper, rapeseed, camellia, corn, sunflower, linseed, perilla seed, sesame, bitter almond and walnut) were purchased from the local supermarkets at Yangling, Shaanxi, China. The choice of the brands was based on the highest consumption among those available on the market. The mesh used for the cell developed in this study was 80 mesh stainless steel wire cloth, with a wire diameter of 0.140 mm and 31% open area (Xi'an Chemical Company, Ltd.). Other mesh sizes evaluated were 40, 60, 100 and 120 meshes. Isopropyl alcohol, toluene, KOH, acetic acid, chloroform, potassium iodide and sodium thiosulfate were purchased from Tianjin chemical company, Ltd. All reagents and chemicals used were of analytical grade.

Instrumentation

A Bruker VERTEX 70 series FTIR spectrometer (Bruker Optics, Germany) equipped with a deuterated triglycine sulfate (DTGS) detector was used for this study.

Preparation of calibration standards and validation samples

The abovementioned 16 kinds of oil samples were allocated randomly based on mass ratio of 1: 1 (two oils) and 1:1:1 (three oils) to produce 25 different mix of oil samples. A total of 41 types of oil samples, which were prepared by accelerating oxidation at 105 °C in an oven for 24 h, were analysed. The oxidation levels of oil samples were determined by using the standard methods, namely, PV (AOCS Official Method Cd 8b-90)[5] and AV (AOCS Official Method Cd 3a-63).[8] The oxidation time was set at two degrees according to AOCS standard, namely, non-oxidised and complete oxidation. A total of 123 samples of various oxidation degrees were obtained and were randomly divided into two sets for calibration and validation. A total of 91 samples were in the calibration set, and the remaining 32 samples were in the prediction set. All samples were sealed, wrapped with aluminium foil and kept at 4 °C in a refrigerator.

Mesh cell selection

To determine the optimum mesh size, different mesh sizes (40, 60, 80, 100 and 120) were selected and compared to complete FTIR detection after deposition of the oils. A sample of edible oil was randomly selected and deposited onto the surface of the mesh cell. The changes of the sample spectra at different standing time points after the sample was placed in the FTIR spectrometer was then obtained. The spectra of samples were recorded for analysis of the baseline and signal to noise ratio.

Spectral acquisition conditions

At ambient temperature (25 °C), spectra were collected via FTIR spectrometer with wavelength ranged from 6000 cm^{-1} to 400 cm^{-1}. The FTIR was operated under transmission mode, and each recorded spectrum was obtained by obtaining the average of 16 scans at a resolution of 4 cm^{-1}.

Instrumental procedures

At ambient temperature, approximately 500 μL of sample was deposited onto the surface of the mesh cell using a micropipette and was subsequently spreaded uniformly using the tip of the micropipette. The viscosity of oil samples was reduced by mixing with hexane to induce their deposition onto the mesh cell. An oil film was formed after the solvent was evaporated. Mesh cells prepared in this manner were placed and maintained in a horizontal position. The spectra of the oil film were obtained using a blank mesh cell background spectrum. The effective path lengths of oil film spectra were normalised to a fixed path length of 0.15 mm by using a path length calibration equation that relates the effective path length to the absorbance at 4334 cm^{-1}.

After each experiment, the mesh cell was disassembled and cleaned by immersion in an aqueous solution of sodium hydroxide (0.03 N) for 10 min in a sonicating bath at 60 °C. The mesh was then rinsed with distilled water, and subsequently, with hexane prior to drying in an oven at 50 °C for 20 min. This cleaning procedure did not result in any visually or spectroscopically observable changes in the meshes.

Discriminant analysis

According to Mahalanobis distance (MD) classification, the calibration sets were developed with a recognition rate same as of the evaluation index model. The model was validated using the validation samples, and the recognition rate of the validation samples was obtained. The basic idea of discriminant analysis involves developing a mathematical model for each category in a certain wavelength range according to the deviation used for known class sample sets (calibration sets). Mathematical models of the unknown sample and various kinds of samples were fitted to calculate the MD between unknown samples and the calibration set to discriminant classification. Stoichiometric spectroscopy analysis was performed using the discriminant analysis method in software TQ Analyst 7.2. The MD calculation formula is as follows:[29,30]

Suppose that there are n samples, and each sample has p indicators. The data matrix is x, and the element x_{ij} denotes the j indexes of the i sample. Assuming that S represents the covariance matrix of the indicators, the average spectrum MD_i category of i samples is as follows:

$$MD_i = (x_i - x_{avg})^T S^{-1} (x_i - x_{avg})$$

MD_i represents a distance (scalar) of i samples to average spectrum (centre sample); x_i is the row vector of the i sample; x_{avg} is the row vector of average spectrum; S^{-1} is the inverse

matrix of the covariance matrix; and $(x_i - x_{avg})^T$ is the transposed matrix of $(x_i - x_{avg})$.

Determination principle

According to AOCS standard, the oils with PV≤10 meq/ kg and AV of ≤0.6 mg/g were defined as non-oxidised oils, whereas those with PV >10 meq/ kg or AV of >0.6 mg/g were defined as oxidized oils. Van de Voort et al. found that the compounds appeared at the absorption region (2700–3650 cm^{-1}) in FTIR spectra contained –OH bonds.[17] The characteristic peaks of hydroperoxides were the regions of PV values. Therefore, the peak height can be used as the basis of PV qualitative analysis of edible oils.

The standard analysis of lipid oxidation was performed by using standard AOCS titrimetric method (Cd 8b-90) to measure PV and AOCS Official Method (Cd 3a-63) to measure AV of edible oil sample. After determining the two values of the sample by titrimetric method, approximately 500 L of sample was deposited onto the surface of the mesh cell to obtain the IR spectroscopy of the oil films using a blank mesh cell background spectrum. The spectra obtained between 3750 cm^{-1} and 3150 cm^{-1} were then analysed with the qualitative model developed based on the MD classification.The recognition rate of validation samples was obtained based on PV and AV.

Statistical analyses

According to MD classification, the discriminant analysis criterion was used to develop qualitative analysis models. The sample recognition rate was used to evaluate the model. All analyses were performed in triplicate, and the mean values were used to express the results. The corresponding peak heights were measured relative to a selected single-point baseline by implementing macros programmed using the Macro/Basic tool provided in Omnic 7.3 (Thermo Electon Inc., Madison, WI). Spectral data processing and statistical analysis were conducted using TQ Analyst 7.2 (Thermo Electron Inc., Madison, WI) and OriginPro 7.5 (Originlab, Northhampton, MA).

Results and Discussion

Mesh size selection

The obtained lipids that were deposited onto mesh cell surface with different mesh sizes were analysed by FTIR, and each sample was analysed for three times. The peak heights at spectra 1712/1650 cm^{-1} (the characteristic absorption peak of AV), 3444/3295 cm^{-1} (the characteristic absorption peak of PV) and 966/925 cm^{-1} (characteristic absorption peak of trans fatty acid (TFA)) for samples on different sizes of meshes were analysed after path length normalisation, and the results are shown in Table 1.

Table 1. Characteristic absorption peaks of AV, PV and TFA compared at different mesh sizes (Mean±SD).

Mesh size	Characteristic absorption peak		
	1712/1650 cm^{-1}	3444/3295 cm^{-1}	966/925 cm^{-1}
40	0.93 ± 0.01^{A}	0.168 ± 0.002^{A}	0.60 ± 0.004^{A}
60	0.91 ± 0.01^{B}	0.167 ± 0.003^{AB}	0.58 ± 0.009^{B}
80	0.87 ± 0.002^{C}	0.165 ± 0.000^{B}	0.59 ± 0.003^{B}
100	0.91 ± 0.003^{B}	0.167 ± 0.002^{AB}	0.58 ± 0.004^{B}
120	0.91 ± 0.005^{B}	0.169 ± 0.001^{A}	0.59 ± 0.003^{AB}

Means within a list indicated by different capital letters are significantly different (LSR test, P<0.01) (n=3).

Table 1 illustrates that mesh size of 80 had highly significant difference compared with other size at 1712/1650 cm^{-1} and had significant difference compared with the mesh size of 40 and 120 at 966/925 cm^{-1} and 3444/3295 cm^{-1}. When the three characteristic absorption peaks with a mesh size of 80 were repeatedly detected, the test result showed the least

fluctuation, and SD was the lowest. The IR transmission characteristics of the mesh showed a substantial dependence on the mesh size, owing to light scattering effects.[26] Consequently, the analysis with a mesh size of 80 to scan IR spectroscopy was the most appropriate.

Influence of standing time on spectrum

A sample of edible oil was selected randomly for deposition onto the surface of mesh cell with the mesh size of 80. The sample was placed in the FTIR spectrometer to obtain the changes of sample spectra at different standing time points. The obtained infrared spectra are presented in Fig. 1.

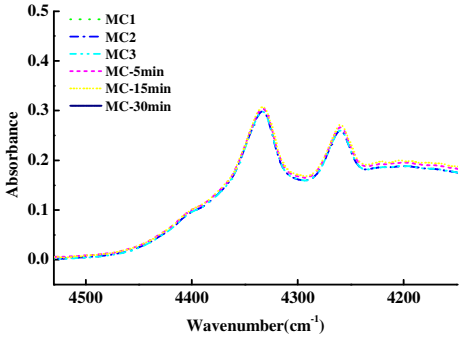
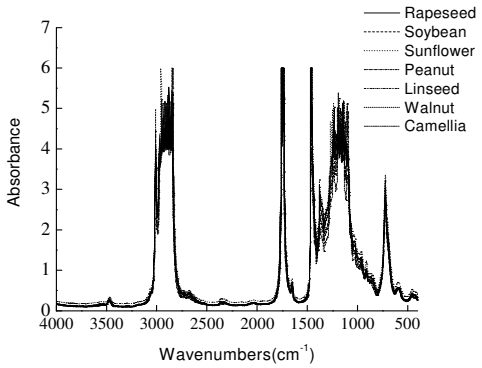


Fig. 1. Influence of standing time on FTIR spectra of samples deposited on mesh cell

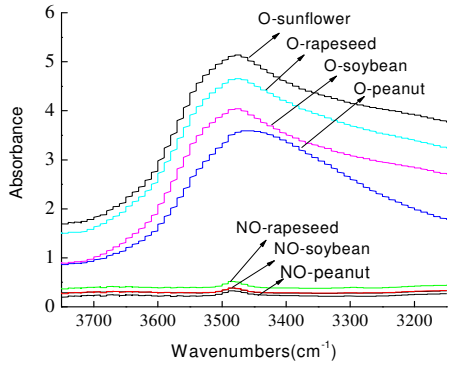
The peak height and peak position of the samples at 4334/4300 cm^{-1} did not fluctuate with changes in standing time (Fig. 1). The peak height at 4334/4300 cm^{-1} and path length of oil films deposited on the test accessory had a high linear correlation. The results showed that the path length of oil films did not fluctuate with the changes of standing time when mesh cell was used as a test accessory, hereby indicated that the film load was stable on the mesh cell (mesh size 80) and the use of mesh cell as the test accessory is feasible

Spectroscopy analysis

A total of 123 spectra were obtained by subjecting the samples to FTIR. The spectra of the seven kinds of oil samples were shown in Fig. 2(a). The spectra comparison of the oxidized and non-oxidized samples range from 3750 cm^{-1} to 3150 cm^{-1} were shown in Fig. 2(b).



(a)



(b)

Fig. 2. Spectra of the seven kinds of samples (a) and comparison of the oxidized (O) and non-oxidized (NO) samples range from 3750 cm^{-1} to 3150 cm^{-1} (b) recorded with a stainless steel mesh cell (80 meshes).

The stainless steel meshes were transparent over the spectral range considered and did not have a baseline tilt caused by light scattering (Fig. 2 (a)). Moreover, because of lower baseline noise compared to other spectral acquisition accessory, the signal to noise ratio was larger, thereby resulted a high sensitivity, which met the determination requirements.

Fig. 2(b) showed the spectra of oil samples in this region (3750 cm^{-1} to 3150 cm^{-1}) had clear distinctions, which could be used to discriminate the oxidized and non-oxidized oils.

Calibration

Mesh cell-based FTIR techniques was applied to investigate the peak height of all 123 oil samples at spectra 3750 – 3150 cm^{-1} (the characteristic absorption peak of PV) after spectrum correction was done based on peak height at 4334/4300 cm^{-1}. According to MD discriminant analysis, qualitative analysis models were developed. The results were shown in Fig.3.

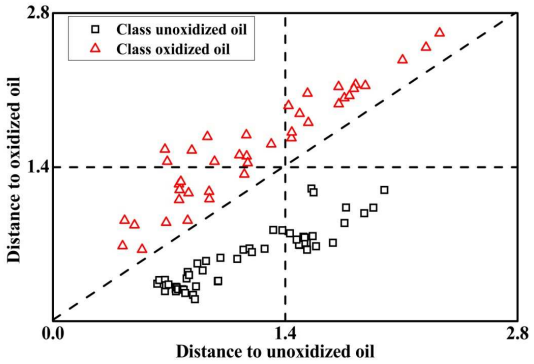


Fig. 3. Distance-discrimination plots for oxidised and non-oxidised oil samples in the calibration set

At wave number range of 3750–3150 cm^{-1}, qualitative analysis models were developed based on the corrected spectral data combined with MD discriminant analysis (Fig. 3). Figure 3 showed that all oxidised and non-oxidised oil samples were well discriminated into the regions of oxidation and no oxidation, with a recognition rate of 100%. Therefore, the corrected distance discriminant analysis method can successfully classify oxidised and non-oxidised oil samples.

Validation

To further validate the model's reliability, a total of 32 samples (16 non-oxidised oil samples and 16 complete oxidation samples) were analysed by discriminant analysis. The results were shown in Table 2.

Table 2. Results of the discrimination analysis for edible oils samples in the validation set.

Sample	Number	Recognition rate/%
Oxidized	16	93.8
Non-oxidized	16	100
All	32	96.9

The PV and AV of six samples were near the ACOS standard (PV ⩽ 10 meq/kg, AV ⩽ 0.6 mg/g) and 5 of them were predicted correctly. Only the one sample was not correctly determined. The particular sample was an oxidised linseed oil with a PV of 10.05 meq/kg and AV of 0.61 mg/g. The difference between the actual PV, AV and the standard were too small, which made the model fail to clearly identify the oxidation status. The possible reason was that the sensitivity of FTIR method is beyond the differences[28,32]. Overall, the high accuracy rate achieved still indicated that using oil characteristic absorption peak detected at the wave number of 3750-3150 cm^{-1} in combination with the discriminate analysis can effectively predict the oxidation status of edible oils.

Conclusions

Mesh cell-based FTIR method combined with discriminant analysis can be used for the qualitative discriminant analysis of edible oils with different oxidation degrees. According to the calibration and validation analysis, the qualitative analysis model was developed in the spectral range of 3750–3150 cm^{-1}. A model which used mesh cell-based FTIR technology combined with MD discriminant analysis was developed. Calibration model recognition rate reached 100%, and the validation model recognition rate reached 96.9%, indicating

that the method was feasible.

Qualitative identification of edible oil oxidation degrees based on mesh cell FTIR procedures is accurate and reliable. Compared to the AOCS official methods, the mesh cell-based FTIR technology is an alternative and innovative tool for faster and cheaper qualitative analysis of edible oil oxidation, and it also considerably reduces the use of toxic organic solvents. When compared with near infrared transmission spectroscopy method [31], this model's establishment is much simpler and requires less spectral pretreatments. The repeated use of mesh cell after each experiment makes it an environmentally friendly method. In conclusion, this method is a highly feasible, green, and fast edible oil oxidation qualitative detection method.

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