APPLICATION OF FOURIER TRANSFORM INFRARED SPECTROSCOPY FOR ANALYSIS, AUTHENTICATION AND MONITORING OF OXIDATIVE STABILITY OF EDIBLE OILS

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BY

ABDUL ROHMAN

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October 2010
Dedicated To My beloved Parents, My wife and My Son
for Their Doa, Patience and Understanding
APPLICATION OF FOURIER TRANSFORM INFRARED SPECTROSCOPY FOR ANALYSIS, AUTHENTICATION AND MONITORING OF OXIDATIVE STABILITY OF EDIBLE OILS

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ABDUL ROHMAN

October 2010

Chairman: Professor Dato’ Yaakob bin Che Man, PhD

Institute: Halal Products Research Institute

Fourier transform infrared (FTIR) has become a powerful analytical technique in the study of fats and oils. The objective of this study was to use FTIR spectroscopy combined with certain chemometrics techniques to analyze, authenticate, and to monitor the oxidative stability of selected edible fats and oils. FTIR spectra combined with principal component analysis (PCA) and cluster analysis using absorbances as variables at 16 frequencies have been successfully used for differentiation of lard (LD). Among sixteen edible fats and oils, extra virgin olive oil, rice bran oil, and chicken fat were close to LD compared with others.

The presence of LD in binary mixtures with beef (BF), chicken, (CF), and mutton fat (MF) was analyzed using FTIR spectroscopy combined with partial least square (PLS) at fingerprint region of 1,500 – 900 cm\(^{-1}\). The coefficients of determination (R\(^2\)) for the relationship between actual value of LD (x-axis) and FTIR predicted
values \((v-axis)\) in BF, CF, and MF were 0.999 0.998, and 0.995, respectively. Frequencies of 1,500 – 1000 cm\(^{-1}\) were selected for quantification of LD in the binary mixtures with selected vegetable oils of canola, corn, extra virgin olive, soybean, and sunflower oils. These frequency regions are also preferred for analysis of LD in quaternary systems using first derivative spectra with \(R^2\) and root mean square error of calibration (RMSEC) values of 0.997 and 0.773 % (v/v), respectively. Furthermore, in food systems using meat ball formulation, LD has been successfully determined at 1,200 – 1,000 cm\(^{-1}\) with \(R^2\) and RMSEC values of 0.999 and 0.442 % (v/v), respectively.

FTIR spectroscopy in combination with PLS and principle component regression (PCR) was also used for quantifying VCO. VCO in binary mixtures with palm oil (PO) is better determined using PLS at combined frequencies of 1,120 – 1105 and 965 – 960 cm\(^{-1}\) with \(R^2\) and RMSEC values obtained were 0.999 and 0.758 % (v/v), respectively. These frequencies were also well suited for quantitative analysis of VCO in binary mixtures with olive oil (OO). Furthermore, frequencies at 1,200 - 1,000 cm\(^{-1}\) using PLS and second derivative spectra was applicable for quantitative analysis of VCO in ternary mixtures with PO and OO.

Authentication analysis of cod liver oil (CLO) from LD was performed using FTIR spectroscopy at frequency 1,035 – 1030 cm\(^{-1}\). In addition, BF, CF, and MF were also successfully determined using PLS at certain optimized frequencies. Discriminant analysis (DA) can successfully classify CLO and CLO adulterated with animal fats at
certain frequency regions. FTIR spectroscopy was also used for authentication analysis of extra virgin olive oil (EVOO) and virgin coconut oil (VCO). FTIR normal spectra along with PLS was preferred over PCR for quantification of studied vegetable oils in EVOO and VCO, except for palm oil which was better determined with first derivative spectra. The $R^2$ values obtained were higher than 0.99 in calibration model. DA successfully classified EVOO and VCO and those adulterated with some vegetable oils. Analysis of fatty acid changes of the authentic oils (CLO, EVOO, and VCO) due to the adulteration practice can complement the FTIR spectral measurements.

FTIR spectroscopy was used to evaluate the oxidative stability of vegetable oils with high mono- and polyunsaturated fatty acids, namely corn, rice bran, soybean, and sunflower oils. The oils were subjected to thermal oxidation at 160 °C for 120 h. Each 12 h interval, the oils were analyzed for its specific absorptivity of conjugated dienes (CDs) and trienes (CTs), $p$-anisidin values ($p$-AV) and FTIR spectra changes at frequencies of 3470, 3008, 1743, 1655, 967, and 721 cm$^{-1}$. FTIR spectral changes at 3008 cm$^{-1}$ can be used to predict the level of oxidation, especially for determination of CDs, CTs, and $p$-AV values.

In conclusion, this study showed that FTIR spectroscopy combined with suitable chemometrics technique can provide reliable analytical tool to analyze and to authenticate edible fats and oils. FTIR spectroscopy could also potentially be used for routine monitoring the oxidative stability of fats and oils.
Abstrak Tesis yang dikemukakan kepada senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

APLIKASI SPEKTROSKOPI TRANSFORMASI FOURIER INFRA MERAH UNTUK ANALISIS, PENGESANAN DAN PEMANTAUAN KESTABILAN OKSIDASI MINYAK MAKAN

Oleh

ABDUL ROHMAN

Oktober 2010

Pengerusi : Professor Dato’ Yaakob bin Che Man, PhD
Institut : Institut Penyelidikan Produk Halal

Kajian ini bertujuan untuk menggunakan spektoskopi Fourier transform inframerah (FTIR) untuk menganalisis, mengesahkan dan memantau kestabilan oksidasi beberapa minyak dan lemak terpilih telah dilakukan.

Kombinasi spektra FTIR dengan analisis komponen utama dan analisis cluster menggunakan absorban sebagai variabel di 16 frekuensi telah berjaya untuk membezakan lemak babi dari minyak dan lemak lainnya. Diantara 16 minyak dan lemak makan, minyak zaitun, minyak dedak padi, dan lemak ayam sangat rapat dengan lemak babi dibandingkan dengan minyak dan lemak lainnya.

Adanya lemak babi dalam campuran dengan lemak haiwan seperti lemak lembu (BF), lemak ayam (CF), dan lemak kambing (MF) telah dianalisis dengan kombinasi spektroskopi FTIR dan kalibrasi “partial least square” (PLS) dalam
lingkungan spectra cap jari iaitu antara 1500 - 900 cm\(^{-1}\). Frekuensi diantara 1500-100 cm\(^{-1}\) digunakan untuk mengesan kehadiran lemak babi dalam minyak sayuran terpilih. Lemak babi dalam campuran empat lemak dapat dikesan pada frekuensi diantara 1500-1000 cm\(^{-1}\) dengan nilai R\(^2\) dan RMSEC yang diperolehi adalah 0.997 dan 0.773 % (v/v). Kehadiran lemak babi dalam bebola dapat dikesan pada frekuensi diantara 1200-100 cm\(^{-1}\) dengan korelasi antara nilai sebenar (paksi x) dan nilai anggaran FTIR (paksi y) ialah y = 0.999x + 0.004, dimana nilai R\(^2\) dan RMSEC adalah 0.999 dan 0.442 % (v/v).

Spektroskopi FTIR juga digunakan untuk mengesan campuran minyak kelapa dara (VCO). VCO dalam dengan PO lebih baik dikesan dengan PLS pada frekuensi 1120 - 1105 dan 965 - 960 cm\(^{-1}\), dengan nilai R\(^2\) dan RMSEC ialah 0.999 dan 0.758 % (v/v). Kombinasi antara frekuensi in dan PLS juga sesuai untuk menentukan campuran VCO dan minyak zaitun (OO). Gabungan frekuensi 1200 - 1000 cm\(^{-1}\) dan PLS dapat digunakan untuk analisis tiga campuran minyak (VCO, PO dan OO).

Keaslian minyak ikan kod (CLO) dari minyak babi dapat dikesan pada frekuensi 1035-1030 cm\(^{-1}\) dengan R\(^2\) dan RMSEC adalah 0.990 dan 1.04 % (v/v). Lemak lembu (BF), ayam (CF) dan kambing (MF) dapat dikesan juga dengan menggunakan PLS pada frekuensi tertentu. Analisis diskriminasi (DA) pula mampu mengklasifikasikan diantara CLO dan campuran CLO dengan lemak haiwan pada frekuensi tertentu. FTIR turut digunakan untuk mengesan EVOO dan VCO. Spektra FTIR normal dan digabungkan dengan kalibrasi PLS lebih terpilih.
dibandingkan dengan PCR untuk mengesan minyak sayuran dalam EVOO. Minyak sawit dapat dikesan dengan lebih baik menggunakan spectra turunan pertama, dengan nilai R^2 lebih tinggi daripada 0.99 pada model kalibrasi. Analisis diskriminasi telah berjaya memisahkan EVOO dan VCO dengan EVOO dan VCO bercampur oleh minyak sayuran ini. Analisis perubahan acid lemak boleh melengkapi data spectra FTIR untuk mengkasi praktik pemalsuan minyak.

Spektroskopi FTIR berpotensi untuk pengukuran kestabilan oksidasi minyak sayuran terpilih. Minyak dengan asid lemak mono tak tepu dan asid lemak poli tak tepu iaitu minyak jagung, minyak dedak padi, minyak soya, dan minyak bunga matahari dikenai panas tinggi (160 °C) dalam oven selama 120 jam. Nilai absorptiviti spesifik diena terkonjugasi (CDs) dan triena terkonjugasi (CTs), nilai anisidin (p-AV), serta spektra FTIR pada frekuensi 3470, 3008, 1743, 1655, 967, dan 721 cm⁻¹ pada minyak tersebut ditentukan setiap 12 jam. Perubahan absorban pada frekuensi 3008 cm⁻¹ dapat digunakan untuk mengetahui tahap oksidasi minyak-minyak sayuran ini.

Sebagai kesimpulan, kajian ini memberi petunjuk tentang kemampuan spektroskopi FTIR untuk melakukan analisis dan autentikasi minyak dan lemak. Tambahan pula, spektroskopi FTIR dapat dicadangkan untuk pemantauan kestabilan oksidasi minyak dan lemak.
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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

**Dato’ Yaakob Bin Che Man, PhD**
Professor  
Halal Products Research Institute  
Universiti Putra Malaysia  
(Chairman)

**Amin Ismail, PhD**  
Associate Professor  
Halal Products Research Institute  
Universiti Putra Malaysia  
(Member)

**Puziah Hashim, PhD**  
Research Fellow  
Halal Products Research Institute  
Universiti Putra Malaysia  
(Member)

---

**HASANAH MOHD GHAZALI, PhD**
Professor and Dean  
School of Graduate Studies  
Universiti Putra Malaysia

Date:
DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously and is not concurrently submitted for any other degree at Universiti Putra Malaysia or other institutions.

____________________
ABDUL ROHMAN
Date: 22 October 2010
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