Chapter 4

Fiber Optic Sensor for the Measurement of Adulteration in Edible Oils

Abstract

A fiber optic sensing system for the adulteration detection of coconut oil and olive oil by less expensive paraffin oil is presented. The fundamental principle of detection is the sensitive dependence of the resonance peaks of a Long Period Grating (LPG) on the changes in the refractive index of the environmental medium, surrounding the cladding surface of the grating.

The performance of the sensor has been tested by monitoring the wavelength and amplitude changes of the attenuation bands of the LPG in response to variation of adulteration levels. The developed sensor is user-friendly, reusable and allows instantaneous measurement of the amount of adulteration without involving any reagents.

4.1 Introduction and motivation

A food article is branded adulterated if any inferior or cheaper substance has substituted wholly or its part in a genuine food article, downgrading the quality of the product. Adulteration of edible oil - blending cheaper oil with premium oil - has always been a profitable business for unscrupulous players. Analysis of the quality of edible oils is of paramount importance in most of the countries. Ensuring the authenticity of the food that we consume has intensified exponentially over the years in every country. Authenticity is a very important quality criterion, especially for edible oils as they are much frequently subjected to rampant adulteration. Higher the price of premium oil, greater is the propensity to adulterate it with low priced oil. The unethical and filthy practice of edible oil adulteration results in the formation of harmful substances in the human organism. The most common adulteration is addition of paraffin oil to expensive edible oils like coconut oil and adulterate virgin olive oil with sunflower oil.

Adulteration of coconut oil with paraffin oil is a common malpractice in South East Asian countries. The much acclaimed properties of coconut oil include its fragrance, taste and presence of medium chain fatty acids, antioxidants, vitamins etc. It is also acknowledged for its good digestibility. Besides cooking purposes, coconut oil is also used widely for medical and industrial purposes in Asian countries. The common adulterants used in coconut oil are liquid Paraffin, Palm oil, palm kernel oil etc. Addition of liquid paraffin is extremely hazardous to human health as it can ultimately lead to several health problems such as liver disorders or even cancer. Up to 20 percent of paraffin oil can be easily mixed with coconut oil and there will not be any notable difference in the smell or colour of coconut oil.

Olive oil is popular edible oil mainly produced and consumed in Mediterranean countries. Although more expensive than other oils, virgin olive oil has many health
benefits. It is important oil that is high in nutritional value due to its high content of antioxidants and monounsaturated fatty acids. Studies have also found that consumption of olive oil can lower the risk of coronary heart disease by reducing bad cholesterol- Low-density lipoprotein (LDL) while raising the good cholesterol- High-density lipoprotein (HDL). It is a common practice today to adulterate virgin olive oil with sunflower oil for financial gain. Sunflower oil is used as the usual adulterant due to its close resemblance to virgin olive oil composition. Adulteration of virgin olive oil with other edible oils also may cause serious health problems.

Different analytical techniques are employed in legitimacy testing of edible oils. Among them are chromatographic methods [1,2], differential scanning calorimetry [3], fourier transform infrared spectroscopy [4], photopyroelectric detection [5] etc. These techniques have the disadvantage that they are expensive, time consuming, require considerable analytical skill and produce hazardous chemical waste. Due to increased public concern and legal requirements, the need for more reliable, rapid and less expensive monitoring and quality checking of edible oil is growing continuously. Fiber-optic sensors offer very attractive solutions in this respect due to their intrinsic merits such as high sensitivity, small size, immunity to electromagnetic interference, high performance, fast response etc. [6]. In 2005, M. Sheeba et al. had reported a fiber optic intensity based evanescent wave sensor for the detection of adulterant traces in coconut oil using an unclad plastic fiber [7]. The main limitation of this evanescent wave sensor is that the cladding and small portion of the core has to be removed manually. This will reduce the mechanical stability of the fiber. In order to avoid this limitation, we are proposing a new LPG based sensor for the detection of adulteration in coconut oil which provides improved sensitivity and robustness.

Unlike FBG, LPG couples light from the fundamental core mode to other forward-propagating cladding modes, produces a discrete set of attenuation bands
in the transmission spectrum of the optical fiber [8-10]. The resonance wavelength of LPGs is a strong function of external perturbations like strain, temperature and surrounding refractive index (SRI) [11-14]. Presence of these external perturbations affects the coupling strength between the core and cladding modes, which could lead to both amplitude and wavelength shift of the attenuation bands in the LPG transmission spectrum. Measurement of these spectral parameters in response to environment, surrounding the grating region, is the basis of sensing with LPGs [15,16]. LPG can be used as an ambient index sensor or a chemical concentration indicator with high stability and reliability [17-20]. With respect to chemical sensing, the resonant wavelength shift and amplitude change of the LPG attenuation bands with the SRI is certainly the most interesting. The RI sensing is very important for biological, chemical and biochemical applications as a number of substances can be detected through the measurements of refractive index.

At present, the refractive index sensing based on the LPG is an extraordinarily important subject in the biochemical sensing area which attracts significant research interest. Here an edible oil adulteration measurement sensor is being demonstrated by exploitation of the sensitivity of LPGs to the concentration of the solution under test. When the edible oils are subjected to adulteration, a change in its original refractive index occurs. Such changes cause corresponding shifts in the resonance wavelength and change in depth (amplitude) of the loss bands in the LPG. Adulteration levels can be measured by analyzing these spectral changes. A complete experimental analysis, on the use of an LPG for adulteration detection in coconut oil and virgin olive oil is being presented. The device performance is analyzed in terms of its sensitivity and resolution. This LPG based sensor possesses the advantages of requirement of small volumes of sample for analysis and provides the response in real time.
4.2 Theory of operation

The LPG operates by coupling the fundamental core mode (i.e. the LP\text{01} mode) to co-propagating cladding modes (LP\text{0m} mode with m = 2, 3, 4, ...) in the fiber. This coupling yields rejection bands around specific wavelengths (resonant wavelengths) in the transmission spectrum of the LPG [21,22]. The wavelength at which the guided mode couples to the cladding modes can be obtained through the phase-matching equation [23,24]:

\[ \lambda_m = [n_{\text{eff,0}}^\text{co} - n_{\text{eff,m}}^\text{cl}] \Lambda \] ...................................................... (4.1)

where \( \lambda_m \) is the resonance wavelength corresponding to coupling to the \( m \)th cladding mode, \( \Lambda \) is the grating period, \( n_{\text{eff,0}}^\text{co} \) is the effective index of the fundamental core mode \( (\text{LP}_{01}) \), \( n_{\text{eff,m}}^\text{cl} \) is the effective index of the \( m \)th order cladding mode \( (\text{LP}_{0m}) \).

The strength of transmission of the attenuation bands [10] can be written as

\[ T_m = 1 - \sin^2 (k_m L) \] ...................................................... (4.2)

where \( L \) is the length of LPG and \( k_m \) is the coupling coefficient for \( m \)th cladding mode. Therefore, the coupled power % depends on \( L \) and \( k_m \). The parameter \( k_m \) however depends on the specific cladding mode and also on the amplitude of refractive index modulation (\( \Delta n_{\text{co}} \)) induced in the fiber core. Changes that occur in the refractive index of the surrounding medium will affect the cladding effective refractive indices and, as a direct consequence, attenuation dips experience both changes in its amplitude \( (T_m) \) and shifts in the resonance wavelengths \( (\lambda_m) \). These spectral changes can be used to measure the external medium refractive index and allows the LPG to be used as a sensor device to determine the concentration of a specific substance in a binary mixture.
The shift of the centre wavelength of the attenuation peaks can occur towards longer or shorter wavelengths based on the SRI. The refractive index sensitivity of the LPG arises from the dependence of the effective index of the cladding mode \( n_{\text{eff},m} \) on the refractive index of the surrounding material. The effect of refractive index of the surrounding medium on the resonant wavelength is expressed by [8,22]:

\[
\frac{d\lambda_m}{dn_{\text{sur}}} = \frac{dn_{\text{eff},m}}{dn_{\text{eff},m}} \left[ \frac{dn_{\text{cl},m}}{dn_{\text{sur}}} \right]
\]

where \( n_{\text{sur}} \) is the refractive index of the surrounding material. For each cladding mode, the term \( \frac{dn_{\text{cl},m}}{dn_{\text{sur}}} \) is distinct and hence an LPG is expected to have a strong dependence on the order of the coupled cladding mode. Higher order cladding modes tend to show greater sensitivity to changes in external refractive index because these modes extend further out into the area exterior to the fiber [10,24].

The spectral change of LPG sensors can be characterized in terms of external RI as follows. If the SRI is lower than the refractive index of the cladding \( (n_{\text{sur}} < n_{\text{cl}}) \), mode guidance can be explained using total internal reflection. In this case, typically strong resonance peaks are observed and the attenuation dips shift towards shorter wavelengths (blue shift) when the external medium refractive index increases up to the fiber cladding refractive index[13,14]. The closer the refractive index of the external medium to that of the cladding, the higher the grating sensitivity and leads to larger wavelength shift. When the value of the ambient refractive index matches with that of the cladding, the cladding layer acts as an infinitely extended medium and thus supports no discrete cladding modes. In this case, a broadband radiation mode coupling occurs with no distinct attenuation bands [25]. In short, when the external RI becomes equal to the RI of the cladding, rejection bands disappear, and the transmission spectrum gets flattened. Once the
SRI is higher than the refractive index of the cladding \((n_{\text{sur}} > n_{\text{clad}})\), the cladding modes no longer experience total internal reflection and Fresnel reflection can be used to explain the mode structure [26]. Whatever may be the value of the external refractive index, a part of the energy is reflected at the interface of the cladding and the external medium. The ratio of the energy reflected will be determined by the Fresnel coefficients. In this case the resonance peaks reappear at slightly longer wavelengths (red shift) compared to those measured with air as the surrounding medium [27]. The depth of each attenuation peak steadily increases with increase in refractive index of the surrounding medium, owing to larger Fresnel reflection coefficients that yield improved reflection at the cladding boundary [28]. So, chemical concentration changes can also be measured by studying the amplitude changes in the LPG attenuation dips.

### 4.3 Experimental setup

In our experiments, a broadband white light source ([Yokogawa] AQ 4305) was used as the light source and the transmission spectrum of the LPG was monitored with an optical spectrum analyzer (OSA) ([Yokogawa] AQ 6319). The LPG sensor head was fixed in a specially designed glass cell with provision for filling the sample and draining it out when desired. We used an LPG with grating length of 21 mm and grating period of 420 \(\mu\)m. The LPG was fabricated at CGCRI using a 248 nm KrF excimer laser source employing point-by-point writing method [10]. The hydrogen loaded photosensitive fiber used has a cladding diameter of 125 micron and a numerical aperture of 0.14. The core and the cladding refractive indices were 1.463 and 1.4563, respectively. There was no protective coating in the grating section, so that the external RI could easily affect the effective refractive index of the cladding modes. The fiber containing the LPG element was connected to the light source on one side and to the OSA on the other side (Fig.4.1). The spectra were recorded on the OSA in the wavelength range 1250–1700 nm.
Drastic changes in performance of the LPG had been noted when there were variations in external characteristics like temperature, bending and strain. To avoid the effect of strain and bending, a special glass cell holder was designed and the fiber was placed stretched and bonded with epoxy at both the end points of the cell such that the grating section was kept at the centre of the cell. For precise measurement, the experimental setup and sample solution temperature were maintained at $25.0 \pm 0.5 \, ^\circ\text{C}$. The resonance wavelength of the LPG dip was measured with the fiber section containing the LPG immersed in samples obtained by mixing paraffin oil and pure coconut oil in different proportions.

Sensor responded to RI changes as soon as samples were introduced to the glass cell. But, to get a stabilized output, all readings were taken one minute after the LPG was immersed in the solution. An Abbe refractometer was employed to measure the sample refractive indices, just after the sample was drained out from the glass cell. The initial spectrum of the LPG in air (Fig. 4.2) is used as reference spectrum for all the sample analysis. The use of this reference spectrum serves two purposes: 1) to remove any trace of each adulterated sample between two different measurements and 2) to assure that the LPG attenuation dip returns to the original wavelength after each sample measurement. At the end of each sample measurement, the grating was cleaned with isopropyl alcohol repeatedly, followed by drying.
properly, so that the original transmission spectrum of LPG was obtained. The changes in the refractive index of the surrounding medium were obtained by increasing the paraffin oil concentration in pure edible oil samples. The refractive indices of pure coconut oil and paraffin oil were found to be 1.450 and 1.454 respectively.

![Figure 4.2: Transmission spectrum of LPG with $n_{\text{sur}} = 1$.](image)

4.4 Results & discussion

4.4.1 Coconut oil adulteration measurement

The dependence of the sensor sensitivity on adulteration in terms of the LPG resonance wavelength shift has been analyzed, while the samples obtained by mixing of paraffin oil and pure coconut oil in different proportions were in contact with the grating. For the grating used in these studies the strongest attenuation peak in air, is located at 1602 nm. Figure 4.3 shows the changes in the wavelength and amplitude corresponding to main attenuation dips (LP$_{05}$ and LP$_{06}$) with increasing concentration of paraffin oil in the mixture with pure coconut oil. The highest order attenuation band (LP$_{06}$) was most sensitive to the surrounding refractive index changes and is shown in Fig. 4.4.
Figure 4.3: Transmission spectra of the LPG surrounded by a mixture of paraffin oil and pure coconut oil in different proportions.

Figure 4.4: Wavelength shift of the $LP_{06}$ mode of the LPG surrounded by a mixture of paraffin oil and pure coconut oil in different proportions.

The refractive indices produced by different oil samples used in the experiments were less than the cladding refractive index of the LPG. If the refractive
index of the surrounding medium is lower than that of the cladding, the fiber supports bounded cladding modes that are maintained by total internal reflection at the surrounding cladding interface. In this case, the surrounding refractive index sensitivity arises from the evanescent wave interaction between the cladding modes and the external medium. This interaction will lead to a strong modification of the central wavelength of the attenuation bands of LPG. For RI values lower than that of the cladding, LPG sensitivity to increasing external index of refraction is evident as a blue shift in the central wavelength of the attenuation band in the grating’s transmission spectrum. The LPG exhibited a total blue shift of approximately 15 nm when the surrounding medium was gradually changed from pure coconut oil to pure paraffin oil sample. For all the adulterated oil sample analyses, the wavelength shifts were measured relative to that of the LPG immersed in the pure coconut oil sample used as a reference fluid. Apart from the wavelength shift with the changes in refractive index of the external medium, LPG also produced a reduction in the peak intensity of the resonance band as reported earlier [18,20].

Figure 4.5 shows the sensitivity of the LPG when used as a sensor for various volume percentage of paraffin oil in coconut oil. It can be seen from the results that the sensor is useful to determine paraffin oil concentration even upto 3% by volume with a good linear sensitivity between 3 % and 50 %. This region is very useful because most of the adulteration and malpractices using paraffin oil are within this range. Repeatability was found to be poor below 3 % adulteration. A spectral shift of 15 nm was obtained in the refractive index range 1.450 to 1.454, which corresponds to an average resolution of $2.66 \times 10^{-4}$ nm$^{-1}$. 
4.4.2 Virgin olive oil adulteration measurement

Measurement of the transmitted signal intensity in a chosen spectral interval was used for olive oil adulteration analysis since all the used samples were with refractive indices higher than the refractive index of the fiber cladding. When the LPG was immersed in pure olive oil sample, the transmission spectrum indicated that the attenuation bands were red shifted compared with those in air. The refractive indices of the binary mixture samples used in the experiments were increased, when we increased the sunflower oil concentration from 0 to 30%. The refractive indices of pure olive oil and adulterated oil samples used in the experiments were varied from 1.4635 to 1.4670. Under these conditions, the sensor exhibited a low sensitivity for measurements in the wavelength domain. So no analysis was conducted for the wavelength shift. The most pronounced effect was the change in the LPG transmission intensity. For intensity measurements the LP06 mode exhibited noticeable amplitude changes and minimal wavelength shifts. So we selected the attenuation dip near 1600 nm for adulteration analysis. As can
be seen from Fig. 4.6, when the adulteration level was increased, there was a very small shift in wavelength and a detectable increase in the intensity of the transmission dip. In short, the depth of each attenuation peak steadily increased when we increased the adulteration level up to 30% sunflower oil in pure olive oil sample.

![Figure 4.6: Transmission spectra of the LPG surrounded by a mixture of sunflower oil and pure olive oil in different proportions.](image)

Figure 4.7 shows the sensitivity of the LPG when used as a sensor for various volume percentage of sunflower oil in olive oil. It can be seen from the results that the sensor is useful to determine sunflower oil concentration even up to 4% by volume with a good linear sensitivity between 4% and 30%. This region is very useful because most of the adulteration and malpractices using sunflower oil are within this range. Repeatability was found to be poor below 4% adulteration. An intensity change of 2.18 dB was obtained in the refractive index range 1.4635 to 1.4670, which corresponds to an average resolution of $1.61 \times 10^{-3}$ dB$^{-1}$. The
LPG sensor sensitivity was around 0.07 dB/vol% of sunflower oil in the measurement range.

Figure 4.7: Transmission spectral intensity changes in the $LP_{06}$ resonance band of the LPG as a function of sunflower oil proportion in olive oil.

4.5 Conclusions

Resonance wavelength shift and amplitude changes of the attenuation bands of the LPG have been monitored to demonstrate an edible oil adulteration measurement sensor. Detection limit of adulteration was found to be 3% for coconut oil-paraffin oil binary mixture and 4% for olive oil-sunflower oil binary mixture. The LPG sensor sensitivity was around 0.15 nm/vol% of paraffin oil in the measurement range. The advantages of this type of grating sensor are their simple fabrication, very easy implementation for measurement, easy interrogation and the fact that it does not involve the use of solvents or toxic chemicals. The developed sensor is user-friendly, reusable and allows instantaneous determination of the percentage concentration of adulterant in an olive oil sample without
involving any chemical analysis. The newly developed sensor also showed good reversibility and repeatability. The measurement system may be used to detect chemical or biological changes in the surrounding media. The simplicity and high sensitivity of the sensor make it worthy for food industry applications, pharmaceutical, chemical and biomedical sensing applications.

This method enables quantitative measurement of adulterant to a level of 3% adulteration with a wide dynamic range. The selectivity of this LPG based sensor can be improved by the identification and application of suitable coating materials which selectively react to a specific type of adulterant.

References


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