Fiber optic sensor for the adulteration detection of edible oils

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A fiber optic sensing system for the adulteration detection of coconut oil and sunflower 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 spectral changes in the grating response due to variation of adulteration levels have been investigated. Detection limit of adulteration was found to be 3% for coconut oil- paraffin oil binary mixture and 4 % for sunflower oil-paraffin oil binary mixture.

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1. Introduction

Analysis of the quality of edible oils is of paramount importance in most of the countries. Edible oils are mixed with low-priced and sub-standard oil and are then palmed off to unwary consumers. This 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 sunflower oil. Coconut oil is widely accepted for its medical, industrial and cooking applications. The much acclaimed properties of coconut oil include its fragrance, taste and presence of medium chain fatty acids, antioxidants, vitamins etc. Sunflower oil is recognized internationally for its health benefits and frying performance. This oil, which is a mixture of monounsaturated and polyunsaturated fats with lower fat levels, is light in taste and has more vitamin E content than any other vegetable oil. Paraffin oil is used as the common adulterant, because of its low price, easy availability and miscibility. Long term usage of paraffin oil is extremely hazardous to human health as it may lead to liver disorder or even cancer.

In recent times, various analytical techniques are used to detect adulteration in different oils. Among them are chromatographic methods, differential scanning calorimetry, fourier transform infrared spectroscopy, photopyroelectric detection 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, immunity to electromagnetic interference, small size, fast response etc. Optical Fiber grating technologies have attracted much attention in recent years due to their numerous applications in fiber optic sensor [1] and communication systems. Fiber gratings are fabricated by creating a region of periodically varying refractive index within the optical fiber core. These gratings are categorized into two types - fiber bragg grating (FBG) and long period grating (LPG) [2,3,4] based on their grating period. LPGs typically have a grating period in the range 100 μm to 1 mm, whereas FBGs have sub-micron period. The FBGs are intrinsically insensitive to the surrounding medium refractive index (SRI), since the light coupling takes place only between well-bound core modes that are well screened from the influence of the SRI by the cladding. Differing from FBG, LPG couples light from the fundamental core mode to the forward propagating cladding modes and results in a transmission spectrum consisting of distinct resonant loss peaks. Various physical changes in the surrounding region such as temperature, strain, bending and refractive index (RI), can cause wavelength shift and change in amplitude of these resonant loss peaks [5,6,7]. Since the LPGs are more useful to sense SRI than sensors based on FBGs, a number of studies on the refractive index sensitivity of LPGs have been conducted in various fields such as bio-chemical analysis, food and chemical industries [8,9]. Besides offering all the advantages of optical fibers, LPGs also offer important key features like wavelength coded information, low back reflection, low insertion loss, high coupling strength, relatively simple and cost effective fabrication, easy interrogation etc.

In this paper an adulteration measurement sensor is demonstrated by exploiting 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 detected by analyzing these spectral changes. 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.

2. Theory of operation

LPGs couple light from the fundamental core mode (i.e. the LP_{01} mode) to the forward propagating cladding modes (LP_{0m} mode with m =2, 3, 4 . . .) in the. The light coupled into the cladding modes eventually get attenuated due to the high loss of the cladding modes. Therefore, the transmission spectrum of the LPG has a series of discrete attenuation bands near the resonance wavelengths. The wavelength at which the guided mode couples to the cladding modes can be obtained through the phase-matching equation [2]:

$$\lambda_m = [n_{eff}^{co} - n_{eff,m}^{cl}]\Lambda \quad (1)$$

where λ_m is the resonance wavelength corresponding to the coupling to the m^{th} cladding mode, Λ is the grating period, n_{eff}^{co} is the effective index of the fundamental core mode (LP_{01}), $n_{eff,m}^{cl}$ is the effective index of the mth order cladding mode (LP_{0m}).The resonance wavelength of LPG is a strong function of external perturbations like strain [10], temperature [11], bending [12] and SRI. Presence of these external perturbations affects the coupling strength between the core and cladding modes, which could lead to both amplitude and wavelengths 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.

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 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 ($n_{eff,m}^{cl}$) on the refractive index of the surrounding material. The LPG based sensor can thus be used for direct measurement of chemical concentrations which determine the surrounding refractive index. In this paper an edible oil adulteration detection sensor based on this LPG theory is demonstrated. The effect of refractive index of the surrounding medium on the resonant wavelength is expressed by [3]:

$$\frac{d\lambda_m}{dn_{sur}} = \frac{d\lambda_m}{dn_{eff,m}^{cl}}\left[\frac{dn_{eff,m}^{cl}}{dn_{sur}}\right] \quad (2)$$

where n_{sur} is the refractive index of the surrounding material. For each cladding mode, the term $\left[\frac{dn_{eff,m}^{cl}}{dn_{sur}}\right]$ 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 [3,4].

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 ($n_{sur} < n_{cl}$), 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 [5,6]. The closer the refractive index to the cladding one, the higher the grating sensitivity and consequently the 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 [13]. In short, when the external RI becomes equal to that of silica, rejection bands disappear, and the transmission spectrum gets flattened. Once the SRI is higher than the refractive index of the cladding ($n_{sur} > n_{clad}$), the cladding modes no longer experience total internal reflection and Fresnel reflection can be used to explain mode structure. In this case the resonance peaks reappear at slightly longer wavelengths (red shift) than those measured with air as the surrounding medium [14]. In such cases the wavelength shift is very small with variation in RI, but changes in the amplitude of resonance dips are large. So, chemical concentration changes can also be measured by studying the amplitude changes in the LPG attenuation dips. The refractive index sensing is very important for biological, chemical and biochemical applications since a number of substances can be detected through the measurements of refractive index.

3. Experimental setup

LPG with grating length of 21 mm and grating period of 420 μm was selected for the experimental testing. The LPG was fabricated at Central Glass and Ceramic Research Institute (CGCRI) using a 248 nm KrF excimer laser source and employing point-by-point writing method. The Ge-B doped single mode photosensitive fiber used had 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. A white-light source ([Yokogawa] AQ 4305) was used as the light source and the transmission spectrum of the LPG was interrogated 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. The fiber containing the LPG element was connected to the light source on one side and to the OSA on the other side (Fig. 1).

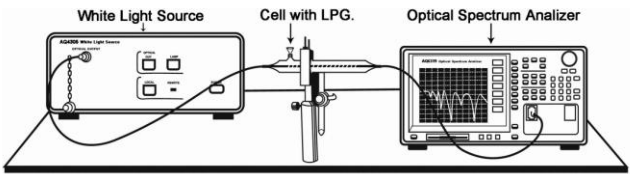

Fig. 1. Experimental setup.

Drastic changes in performance of the LPG were noted when there were fluctuations in external characteristics like strain, temperature and bending. 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 so 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 ± 0.5 °C. The resonance wavelength shift and amplitude changes of the LPG attenuation dip were measured with the fiber section containing the LPG immersed in samples obtained by mixing paraffin oil and pure edible oil samples 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. 2) is used as reference spectrum for all the sample analysis. The use of this reference spectrum serves two purposes: to remove any trace of each adulterated sample between two different measurements and 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 change in the refractive index of the surrounding medium was obtained by increasing the paraffin oil concentration in pure edible oil samples.

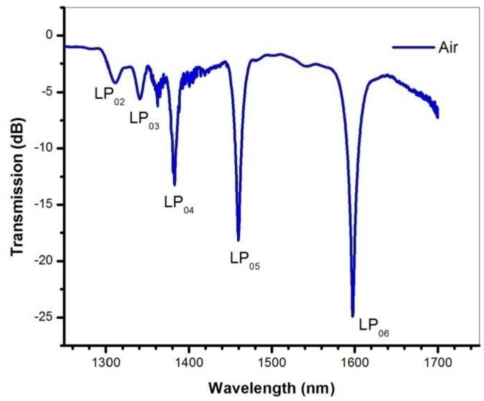

Fig. 2. Transmission spectrum of LPG in air.

4. Results and discussion

A. Sensitivity of the LPG to ambient refractive index changes

The changes of the LPG transmission spectrum with the changes in the RI of the external medium are shown in Fig. 3. Attenuation bands in the range of 1250– 1700 nm related to the cladding modes LP_{02}, LP_{03}, LP_{04}, LP_{05} and LP_{06} have been investigated. When we changed the SRI from 1 to 1.456, the principal effect was a blue shift of these attenuation bands, as discussed in the theory. Each mode has the maximum wavelength shift, when the SRI reached near the RI of cladding. The higher order cladding modes, LP_{05} and LP_{06} exhibited longer displacements compared to lower order modes. The LP_{06} mode was most sensitive to the surrounding refractive index change and exhibited a blue shift of approximately 128 nm. When the SRI value (1.456) matched with that of the fiber cladding RI, almost all cladding modes disappeared and a flat transmission spectrum was obtained, as per the LPG behavior explained in the theory. With an ambient index higher than that of the cladding, the resonance peaks reappeared at a wavelength slightly longer than that measured in air and the strength of the attenuation peaks increased with increasing SRI.

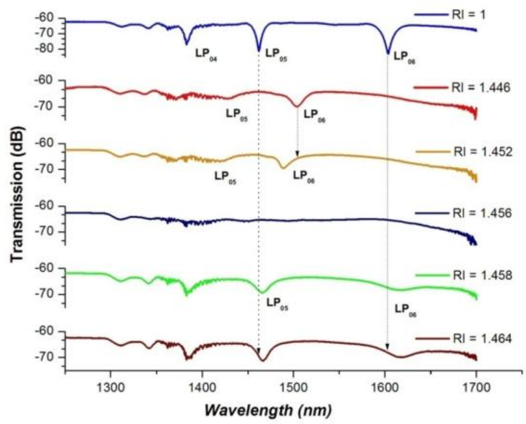

Fig. 3. Progression of transmission spectra of the LPG for increasing external refractive indices.

B. Coconut oil adulteration detection

The dependence of the sensor sensitivity on coconut oil adulteration in terms of the LPG resonance wavelength shift has been analyzed, while the samples obtained from the mixture of paraffin oil and pure coconut oil in different proportions were in contact with the grating. The refractive indices of pure coconut oil and paraffin oil were found to be 1.450 and 1.454 respectively. For the grating used in our studies the strongest attenuation peak (LP_{06}) in air, is located at 1602 nm. Fig. 4 shows the changes in the wavelength and amplitude corresponding to this major attenuation dip, with increasing concentration of paraffin oil in the mixture with pure coconut oil. The refractive indices of the mixture of different oil samples used in this experiment were less than the cladding refractive index of the 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 coconut 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 with increasing RI.

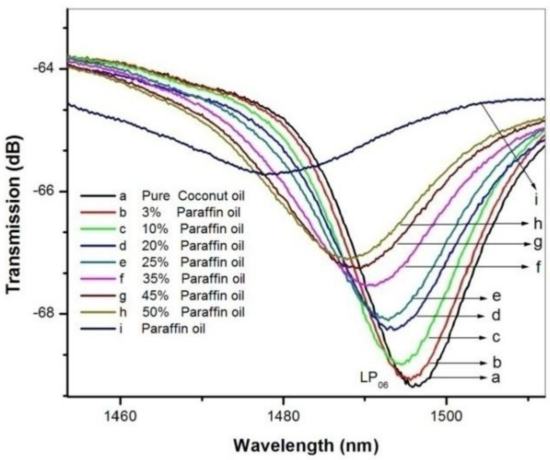

Fig. 4. Transmission spectra of the LPG surrounded by a mixture of paraffin oil and pure coconut oil in different proportions.

Fig. 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 adulteration 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 2.66×10^{-4} nm^{-1}. The LPG sensor sensitivity was around 0.15 nm/vol% of paraffin oil in the measurement range.

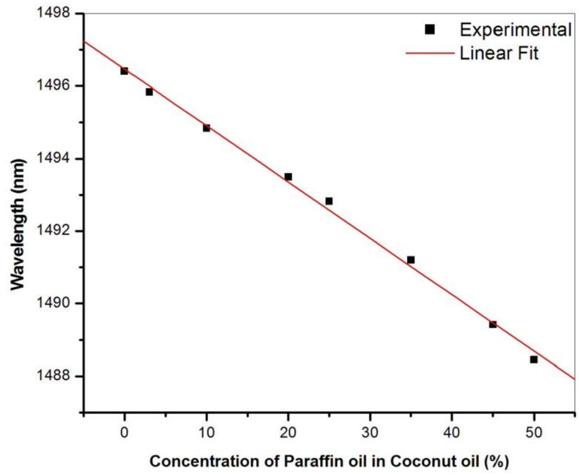

Fig. 5. Peak positions of the LP_{06} resonance band in the LPG transmission spectra as a function of Paraffin oil proportion in coconut oil.

C. Sunflower oil adulteration detection

Measurement of the transmitted signal intensity in a chosen spectral interval was used for our sunflower oil analysis since all the used samples were with refractive indices higher than the refractive index of the fiber cladding. The refractive index of pure sunflower oil, used in our experiment was found to be 1.468. When the LPG was immersed in pure sunflower oil sample, the transmission spectrum indicated that the attenuation bands were reappeared and slightly red shifted compared with those in air. The refractive indices of the binary mixture samples used in our experiments were decreased, when we increased the paraffin oil concentration from 0 to 50 %. 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 LP_{05} mode exhibited more sensitivity than LP_{06} mode. So in this case, we selected the attenuation dip near 1466 nm for adulteration analysis. As can be seen from Fig. 6, when the adulteration level increased, there was a very small shift in wavelength and a noticeable decrease in the intensity of the transmission dip. In short, the depth of each attenuation peak steadily decreased when we increased the adulteration level up to 50% paraffin oil in pure sunflower oil sample.

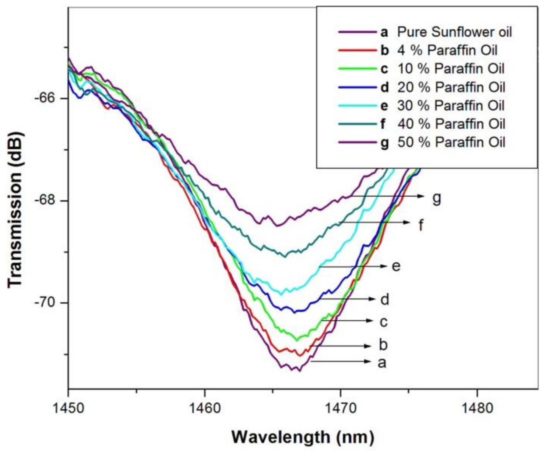

Fig. 6. Transmission spectra of the LPG surrounded by a mixture of paraffin oil and pure sunflower oil in different proportions.

Fig. 7 shows the sensitivity of the LPG when used as a sensor for various volume percentage of paraffin oil in sunflower oil. It can be seen from the results that the sensor is useful to determine paraffin oil concentration even upto 4% by volume with a good linear sensitivity between 4 % and 50 %. Repeatability was found to be poor below 4 % adulteration. An intensity change of 2.76 dB was obtained in the refractive index range 1.468 to 1.460, which corresponds to an average resolution of 2.9×10^{-3} dB^{-1}. The LPG sensor sensitivity was around 0.06dB/vol% of paraffin oil in the measurement range.

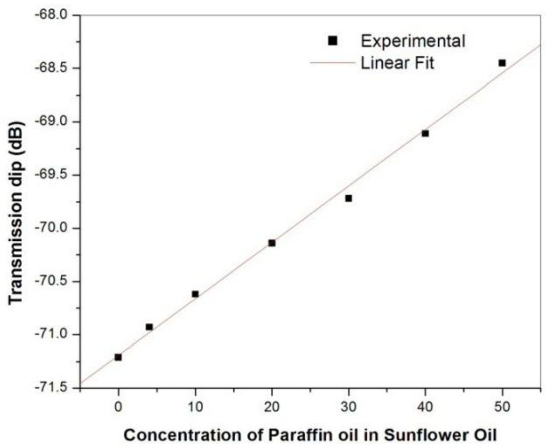

Fig. 7. Transmission spectral intensity changes in the LP_{05} resonance band of the LPG as a function of Paraffin oil proportion in sunflower oil.

5. Conclusion

Resonance wave length shift and amplitude changes of the attenuation bands of the LPG have been monitored to demonstrate an edible oil adulteration measurement sensor. 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 edible oil sample without involving any chemical analysis. The measurement system may be used to detect chemical or biological changes in the surrounding media. This sensor can also be used for foodstuff quality control and industrial applications.

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