Fluorescence-Based Determination of Olive Oil Quality Using an Endoscopic Smart Mobile Spectrofluorimeter

Md Arafat Hossain, *Member, IEEE*, John Canning, *Member, IEEE*, and Zhikang Yu

***Abstract*—The application of self-contained field-portable, internet connected spectroscopic diagnostics in food analysis using a fibre endoscopic smart fluorimeter is reported. A UV-induced fluorescence measure of the quality of olives oils, distinguishing between extra virgin and others, is identified and demonstrated with a smartphone platform. When excited at $\lambda \sim 370$ nm, the extra virgin olive oil fluoresces red at $\lambda \sim 670$ nm. Notably, other oils do not fluoresce red but rather blue, consistent with degradation of the chlorophyll in the oil. Artificial refinement employed in some of the commercial products removes the red emission providing a simple method for distinguishing extra virgin olive oil from all other oils. A smartphone endoscopic fluorimeter is designed and constructed that measures the emission band $\Delta\lambda \sim (400 – 700)$ nm with $\lambda \sim 370$ nm excitation. The instrument is used to characterise the fluorescence of the oils. Photo-degradation over time for extra virgin olive oil under room lights is observed, demonstrating the origin for the decomposition of extra virgin olive oil in transparent bottles. Extra virgin olive oils are also susceptible to thermally degrade more than refined oils.**

***Index Terms*—Lab-in-a-phone, smartphone spectrometer, optical fibre spectrometer, fluorescence, food sensing, olive oil, extra virgin olive oil, photo-degradation, thermal degradation.**

I. Introduction

Global trade means quality assurance of food stuffs is increasingly a global concern. The mechanism and standards in developed countries are being challenged by the logistical reach required to ensure integrous supply to other regions. Confidence in knowing where food originates and the standards surrounding their growth, identification and transport is a global driver for the purchase of food from countries like Australia and New Zealand. It is being undermined by substantive failures in monitoring and law enforcement over both fake food products and rebadging of genuine foodstuffs outside the legal jurisdictions of developed countries. Australia and New Zealand enjoy a high international reputation for food quality and Australian farming produce, from meat, dairy and vegetable to more gourmet products, arguably the most sought after in the world. Organic food production in particular is enjoying heightened interest ironically in part driven by the explosive growth in fake food products in developing countries with growing middle class incomes, such as China, Indonesia and India. Maintaining this reputation and ensuring standards are met and are traceable requires new global standards and reach. Technology around the Internet-of-Things (IoT) can enable this by ensuring replicable global monitoring and diagnostics through new accredited internet distribution channels from the farm, to the distribution ports and retailers and finally the end consumer, irrespective of where they are. Whilst both the network and food standards have to be global in reach, this technology has to be locally field-portable, accessible and easy to use as well as directly and robustly linked to the global network. This changing and increasingly global internet based distribution model supported by new technology requires new quality assurance models that provide data and identification in real time and on-line supported by international bodies. Smart device based technology will underpin this new international era [1], [2].

Among various dietary foods of global gourmet value, vegetable oils such as olive oils are the most commonly sought. As well as simply identifying the source of these foods to verify the level of quality, concerns have been raised of prevalent fake oil distribution passed off as extra virgin olive (EVO) oil [3]. EVO oil is one of a few genuine sources of monounsaturated fatty acids, vitamin *E* and chlorophyll (Chl) [4], attributed to healthy eating and a key ingredient of the Mediterranean diet associated as being optimal for human consumption [5], [6]. EVO oil is cold pressed to preserve its natural ingredients with minimal degradation involved, commanding premium prices. However, some EVO oils, including fake products, as well as refined olive (RO) oil products, have characteristics and chemical composition that are difficult to detect with simple visual inspection. These degraded products can instead have highly oxidative molecules that can create adverse health effects if consumed too often [7]. Clearly, there is a specific need for instrumentation that can measure and corroborate acceptable focus on olive oils and demonstrate novel smart device technology to address this challenge. In doing so, we show how such technology forms the basis for a new approach

This work is supported by the grants from Australian Research Council (ARC DP140100975), the Edmund Optics Education Award and private funding of J. Canning.

M.A. Hossain, J. Canning and Z. Yu are with the *i*nterdisciplinary Photonics Laboratories (*i*PL), School of Chemistry, The University of Sydney, NSW 2006 and School of Electrical and Data Engineering, The University of Technology Sydney (UTS), NSW 2007, Australia (e-mail: arafat.usyd@gmail.com; john.canning@uts.edu.au; zhikang.yu@yahoo.com).

M.A. Hossain is also with the School of Electrical and Information Engineering, The University of Sydney, NSW 2006, Australia.

Deleted: Quality Assurance of
Formatted: Highlight
Deleted: s
Formatted: Highlight
Deleted: assurance
Deleted: with
Formatted: Highlight
Formatted: Highlight
Deleted: observed
Deleted: with the
Deleted: diet
Formatted: Highlight

to quality assurance that has broader agricultural application and is compatible with the Internet distribution market.

II. Characterising Olive Oils

A number of non-destructive methods including machine vision, hyperspectral imaging, ultrasound measurement and acoustic emission and visible to near infrared spectroscopy are used for regular and on-site assessment of food's quality [refs]. With machine vision, other work uses an optical source to illuminate the sample and an imaging unit to capture the sample image [8], [9]. Appropriate computer hardware and software processes the image from its colours, texture, shapes, and sizes. Hyperspectral imaging provides spectral information of a food's constituents [10]-[12]. Techniques using acoustic and ultrasound measurements are also becoming popular, as they are cost-effective and efficient tools to evaluate the quality of many agricultural items including fruits and vegetables [13], [14]. These use a sound unit, absorption medium and a technique to determine the phase oscillation created by the sounds when crushing the food. Similar to hyperspectral imaging, spectroscopic measurements also produces a unique signature of a particular food item but the spectrum produced here is presented as the intensity of light versus wavelength. Different forms of this analysis include absorbance, fluorescence and reflectance spectroscopy using visible to near infrared light to spectrally investigate food quality [15]-[22]. Among them, fluorescence and absorption spectroscopy are widely used techniques to characterize vegetable oils [19]-[22]. Fluorescence spectrum of a particular olive can make known the presence of specific fluorophores that bears significant information about its cultivation and harvesting methods, packaging and storage condition and/or even the constituent elements. The fluorescence spectrum can be represented as a unique fingerprint of a particular oil type with overlapping fluorophores emission that requires deconvolution and complex data analysis [19], [20]. Sometimes statistical analysis based on principle components are used to process large number of oil samples for identifying both inter-class and intra-class variations [19], [21]. This processing, analysing and reporting to consumers often involve time-consuming and expensive tools therefore problem-specific. Further limitations may arise where additional actions are needed in sampling such as solubilisation in liquids, filtration, and pre-treatment with other materials. There are increasing reports of micro spectrometer devices, some of which are fibre-optic based, that fill this gap [21]-[25].

Smart device instrumentation [26] such as smartphone lab-in-a-phone technology – phone instrumentation based on colorimetry – is finding new and novel applications, including IoT-led biomedical and agricultural diagnostics such as for food pathogens and infectious diseases [27]-[33]. A mobile phone was used to assess the quality of various foods and beverages including banana ripeness [34], pH in sweat and saliva [35], grape variety and oxidation status of red wine [36], total coliform and *E*-coli bacteria [37] and turbidity and bromide ions in drinking water samples [38]. In order to assist colorimetric detection, additional disposable lateral flow-through paper/microfluidic-based strip was were integrated into the smartphone platform that significantly reduce the complexity associated with sample processing [39]. Further advance measurements are now increasingly relying on spectroscopy based analysis [40]-[44]. All of these applications can be adapted to the lab-in-a-phone platform merging photonics with smartphones [2], a technology that is rapidly benefiting from integrated LEDs, lasers, new generation optical chips that are potentially written into the smartphone screen [42], [45], infra-red CMOS imaging chips [46], and quantum single photon sources such as those made from self-assembled nanoparticles [47]. Combined photonic multiple functionality in a smartphone is now also possible, after having first been demonstrated as a "dual" absorption and fluorescence spectrometer all-in-one phone [43], using the light and camera source of the phone. Of particular relevance to agricultural applications is the use of optical fibre technology [44] allowing light collection from difficult-to-access places in the field simultaneously removing unwanted stray illumination. This allows reproducible, weather insensitive, measurements from surfaces of foods (liquid or solid) or any arbitrary source, greatly opening-up the potential of applied smart-device technology.

In this work, the advantages of our previously reported optical fibre smartphone absorption spectrometer [44] are retained whilst adding florescence capability by integrating an array of ultra-violet (UV) LEDs all powered by the same device battery. The circuit minimises power consumption and maintains reasonable green credentials of the technology. Using this enhanced instrument, visible fluorescence spectra of the olive oils can be collected remotely to identify the oxidation components within the oils and auto-archived to the web. In particular, a unique red fluorescence is observed in EVO at λ_{em}~ 670 nm due to chlorophyll-*a* (Chl-*a*) that naturally comes from the fresh olives during pressing the fruit. On the other hand, the Chl-*a* emission band is found absent in RO and other vegetable oils. Chl-*a* is particularly a key parameter for the health of many ecological systems including the waterways and is regarded as fundamental biomolecule in photosynthesis. Chl-*a* is characterised by its distinctive green pigment, consisting of a magnesium porphyrin structure that shows emission in the red portion of the visible spectrum when excited by UV/blue light. The presence of Chl-*a* is essentially used as a marker of quality indicating the freshness of many food items including some fruits, vegetables and oils. The most essential property of Chl-*a* in olive oils is its anti-oxidative nature that offers resistance against oxidation in dark environment. Therefore, the presence of Chl-*a* can be used also as a marker of oxidization level and hence quality indicator of the olive [48]. Another distinctive emission between the refined and extra virgin olive is observed at λ_{em} ~ 452 nm that comes from the oxidation compounds in oils and strongly exists in refined products as compared to the extra virgin olive [19]. It is also observed that the relative intensities are robust to thermal treatment but change with photo-degradation and novel approach to quickly identify the quality of extra virgin olive oil is demonstrated.

III. Device Instrumentation

The smartphone optical fibre spectrofluorimeter described here is made of a 3D printable attachment block fitted with the rear facing camera unit of the smartphone that holds all optics

Formatted ...
Deleted: .
Deleted: , [21]-[24]… a technology that is rapidly benefiting fro ...
Formatted ...
Formatted ...
Formatted ...
Deleted: The instrument working on the mac
Deleted: principle generally
Formatted ...
Formatted ...
Deleted: on board
Formatted ...
Deleted: They can be operated through… an a ...
Formatted ...
Deleted: application that
Formatted ...
Deleted: The h
Formatted ...
Deleted: technique also
Deleted: uses an optical source and detector unit but the image ...
Formatted ...
Deleted: figure of
Formatted ...
Formatted ...
Deleted: When illuminating the food sample, electromagnetic ...
Formatted ...
Deleted: t
Formatted ...
Deleted: system
Formatted ...
Deleted: s
Formatted ...
Deleted: 24
Deleted: ,
Formatted ...
Deleted: which are found mostly useful within
Formatted ...
Deleted: -…ed span…ight of the spectrum t ...
Deleted: or even the constituent chemical composition
Formatted ...
Formatted ...
Deleted: Spectroscopic analysis, particularly f
Formatted ...
Deleted: ,…areis ...
Formatted ...
Deleted: a commonly
Formatted ...
Deleted: 8
Formatted ...
Deleted: 11
Formatted ...
Formatted ...
Deleted: Specifically, fluorescence spectroscopy identifies the ...
...
Formatted ...
Formatted ...
Formatted ...
Formatted ...
Formatted ...

for light propagation, collection and dispersion. The position and alignment of each component has been determined by optical design and a custom designed smartphone app runs the fluorescence measurements. A schematic of the design and operation is illustrated in Fig. 1.

A. *Endoscopic fluorimeter design and fabrication*

The optical layout and 3D design of the endoscopic mobile fluorimeter are shown in Fig. 1(a) and (b) respectively. The fluorescence excitation sources are ultra-violet (UV) LEDs (Model No. FD-50TW20, λ_{exc}= 370 nm, $\Delta\lambda_{3dB}$= 30 nm), powered from the smartphone (Samsung Galaxy S4, Model I9500, Octa-core CPU, 1080x1920 pixels AMOLED display, 13 MP rear camera and 2600 mAh battery) via its micro USB port that can deliver a maximum of 500 mA current at 5 V. A flexible fibre bundle probe (Edmund Optics, FiberScope, L= 60 cm) integrated into the smartphone captures fluorescence and avoids ambient illumination. The fibre bundle probe consists of two sets of fibres; illumination and collection fibres. The illumination fibres are assembled inside the bundle probe to transmit light from the source to the sample. Fluorescence is collected at the collection fibre bundle centre of the endoscope; a microscope objective, in-built at the end of the fibre bundle, increases light collection. To avoid UV degradation of the endoscope fibres, instead of sending the light through the illumination fibres, three UV LEDs are placed at the end of the endoscope near the sample. A customised cap fitting holds the LEDs with wires wound around the endoscope. These parallel connected LEDs are evenly spaced to uniformly illuminate the sample surface. A series resistor (R = 22 Ω, P = 2 W) limits current to the LEDs. To ensure a constant distance of the sample from the endoscope, the cap periphery is extended further, l = 1.0 cm. The collected light at the receiver end is collimated and dispersed onto the smartphone camera using a low-cost, but somewhat inefficient, digital versatile disc (DVD) as a diffraction grating (Philips, G ~ 722 lines/mm). An emission slit, w = 0.7 mm determines the spectral resolution obtained ($\Delta\lambda$ = 2.0 nm) [44]. The resolution can be improved further by using a slit of lower w, but sacrificing the light intensity reaching to the detector. A cylindrical lens (Edmund Optics, d = 25 mm, f = 25 mm) is also used to improve light collection per pixel onto the detector. Both the cap and the spectrometer package for a smartphone are designed on AutoCAD and prototyped on a fused deposition modeling (FDM) based 3D printer (Zortrax, M200) using low-cost ABS plastic (Fig. 1(c)).

B. *Application software (app)*

A customized smartphone application (app) is developed in Android platform. It performs all measurements and allows ready sharing of the data as well as archiving into the cloud. The smartphone app consists of two functional screens – one for imaging the diffracted light and the other for plotting spectrum as intensity versus wavelength (I vs λ). In order to produce accurate spectrum that is comparable to the standard spectrometer, the diffraction image is calibrated by considering both wavelength and intensity distribution across each pixel. A detail of the step-by-step calibration procedure is discussed in [2], [44]. To clean the spectra, the intensity was calculated after averaging the value from a width of 15 pixels. The plotted spectra can be used to identify and monitor a particular emission band in real-time. For example, the level of Chl-*a* can be known directly by looking at the red emission band [19]. After selecting from the menu option the app allows the user to find ratios of different emission bands and identify correlation between them. This is useful to classify different oils from a known function of calibrated co-efficient. The measurement report can be displayed on the mobile screen or archived in time and location (GPS) either to the smartphone memory or to a cloud service or computer server via the Internet.

C. *Device operation*

The fiber bundle probe is flexible enough for endoscopic operation making the mobile spectrofluorimeter smarter and user-friendly for hand-held and field-portable operation. In order to avoid the effect of container material on fluorescence emission, firstly, a 20 mL of oil sample is transferred to clear glass vials (21 mL) as shown in Fig. 2(a). In the second step, the user needs to butt the fiber bundle cap end against the surface of the glass vial and run the mobile app following the instruction provided inside the app. By running app, it allows the user to capture the image of the fluorescence and plot the diffracted light as a spectrum. Analysis of sample in the second screen of the app allows the user to identify the type and grade of the oil samples by selecting and automatically comparing intensities at different wavelengths. The results of each oil sample can be stored in the phone's local storage as well as shared to others.

Deleted: 24…4]. To clean the spectra, the intensity was calculated after averaging the value from a width of 15 pixels. The plotted spectra can be used to identify and monitor a particular emission band in real-time. For example, the level of chlorophyll-*a* (…hl-*a*)…can be known directly by looking at the red emission band [8 …

Formatted: Highlight

Deleted: principle …s illustrated shown …

Moved (insertion) [1]

Deleted: -….n the app allows the user to find ratios of different emission bands and identify correlation between them. This is useful to classify different oils from a known function of calibrated co-efficient. The measurement report can be displayed on the mobile screen or archived in time and location (GPS) either to the smartphone memory or to a cloud service or computer server via the Internet. ¶ …

Formatted: Indent: First line: 0.36 cm

Formatted …

Deleted: micro USB port (5 V, 500 mA) port of the

Formatted …

Formatted: Highlight

Moved (insertion) [2]

Formatted: Highlight

Formatted: Highlight

Deleted: compare their visual appearance, sample of each

Formatted …

Deleted: type was transferred

Deleted: a

Deleted: of identical size …21 mL) as shown in Fig. 2(a)depicted in Fig. 2(a) …

Formatted …

Deleted: To avoid UV degradation of the endoscope fibres,

Formatted: Highlight

Deleted: UV

Formatted …

Deleted:

Formatted: Not Strikethrough

Deleted: within a

Formatted …

Deleted: Fluorescence is collected at the fibre bundle centre of the endoscope; a microscope objective, in-built at the end of the fibre bundle, increases light collection.

Deleted: -

Formatted: Highlight

Deleted: optical

Formatted …

Deleted: Samsung Galaxy S4

Formatted: Highlight

Deleted: using

Formatted: Highlight

Deleted: ing…with …

Formatted: Highlight

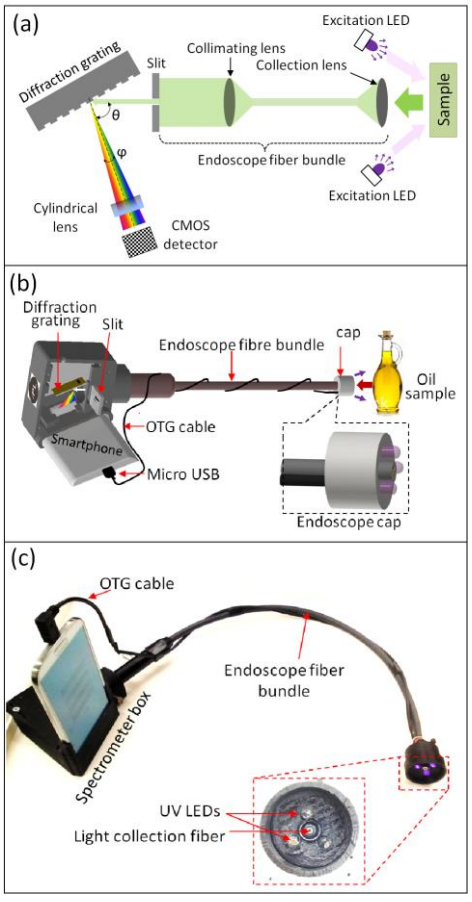


Fig. 1. Configuration of the smartphone endoscope spectrofluorimeter.(a) Optical layout; (b) 3D AutoCAD 3D design of the fluorimeter and (c) the 3D-printed version of the fluorimeter installed on a smartphone [2].

IV. Analysis of Olive Oils

A. Samples

Table. 3.1: Comparison of fluorescence intensities measured at 452 and 670 nm for different types of olive oils.

Oil type	I_{452} (a. u.)	I_{670} (a. u.)
Extra virgin olive	4.2±1.0	18.4±0.8
Refined olive	24.5±1.5	0.8±0.7
Canola	47.7±2.5	0.7±0.5
Peanut	19.6±1.2	1.1±0.7
Rice bran	38.1±2.6	1.1±0.6
Sunflower	29.7±0.9	1.1±0.7

Vegetable oils of different types were collected from a local supermarket. The oil samples include EVO (two different brands), RO, canola, peanut, rice bran and sunflower oils. Amongst them, olive oil is of the particular preference to consumers due to its health benefits such as protection against strokes, osteoporosis, diabetes, Alzheimer's and many others [49]. Olive oil is also considered as a strong source of monounsaturated fatty acid which naturally comes from the olive fruit when the oil is pressed.

Both the physical and chemical properties are important to characterize an oil type. Flavor and colour is considered as key physical indication of good oil. The flavor range from mild to very strong and appearance vary upon the presence of carotenoid and chlorophyll derivatives. Chemically the oil is classified based on the presence of acidity and the process involved in oil extraction. The olive oil which is graded as "virgin" is usually cold pressed – a mechanical process that involves no heat and contains a very low level of acidity (less than 2%). This grade of olive oil comes from the first pressing of the olives therefore preserves most of its natural constituents including the vitamins (A, B_2, K, D and E) and photochemicals [49]. In another grade of olive oil that uses heat and chemicals to press the olive residue subsequently is labeled as "pure" or "refined" oil. The oils labeled as "extra virgin" must be free from refined oils and contains much higher degree of potent items, which worth a premium price.

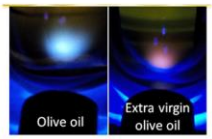
B. Olive oil classifications

A vegetable oil of particular brand have its unique properties, specific uses and customer preferences but most do not offer the health benefits attributed to olive oil. Some are instead considered detrimental with long periods of use. The noticeable variations among the suppliers makes visual inspection and classification extremely difficult, worsened when chemicals such as chlorophylls are introduced artificially. To identify the unique characteristic of each vegetable oil that arises from its constituent chemicals, fluorescence spectra of each sample were measured. To excite and collect the fluorescence emission, the fibre bundle probe is butted against the side wall of the glass vial containing the oil sample. This way of sample placement allows the instrument collecting the front-face fluorescence of sample and therefore, reducing self-absorption by the oil [50].

From the measurement of emission spectra (Fig. 3), distinctive fluorescence emissions were observed between the olive oil and all other vegetable oils. In particular, significantly weaker blue emission at λ_{em} ~ (452 ± 40) nm and strong red emission at λ ~ (670 ± 20) nm, which correspond to oxidation and Chl-*a* compounds [19] in olive, are found in virgin oil as compared to the refined and other oil types. By analysing these dominating emission bands, different values of intensities, I_{452} and I_{670} are calculated for each oil sample and the results are compared in Fig. 4. The smart app algorithm compares I_{452} and I_{670} to determine the oil types automatically and finally display results. The results are consistent with the spectra measured using the benchtop instruments in [19], [50], [51].

Moved up [2]: In order to compare their visual appearance, sample of each type was transferred to clear glass vials of identical size (21 mL) as depicted in Fig. 2(a).
Deleted: 28
Deleted: 29
Deleted: ¶
Deleted: Chl
Deleted: 31
Formatted: Highlight
Deleted: considerably
Formatted: Highlight
Moved up [1]: -on the app allows the user to find ratios of different emission bands and identify correlation between them. This is useful to classify different oils from a known function of calibrated co-efficient. The measurement report can be displayed on the mobile screen or archived in time and location (GPS) either to the smartphone memory or to a cloud service or computer server via the Internet. ¶
Deleted: -on the app allows the user to find ratios of different emission bands and identify correlation between them. This is use ...
Deleted: MEASURING
Deleted: λ_{em} ~
Deleted: 452 nm
Formatted: Highlight
Formatted: Highlight
Formatted: Highlight
Deleted: areis
Deleted: ing
Deleted: to
Formatted: Highlight
Formatted: Font: Italic, Highlight
Formatted: Highlight
Deleted: 8
Deleted: is
Formatted: Highlight
Formatted: Highlight
Moved (insertion) [7]
Formatted: Highlight
Deleted: at λ ~ (452 ± 40) nm and λ_{em} ~ (670 ± 20) nm
Deleted: to
Deleted:
Formatted: Highlight
Deleted: type
Formatted: Highlight
Formatted: Highlight
Deleted: status of the oil
Formatted: Highlight
Deleted: ¶
Deleted: ¶ ...
Formatted: Indent: First line: 0 cm

(a) Under normal ambient light (identical vials)



(b) Under UV light

Fig. 2. Oil samples of different types. Appearanceof different oil types in 21 mL clear glass vials of identical size at - (a) normal fluorescence lamp illumination (7 different brands), and (b) UV illumination (RO and EVO oils)from the fibre endoscope probe [2].

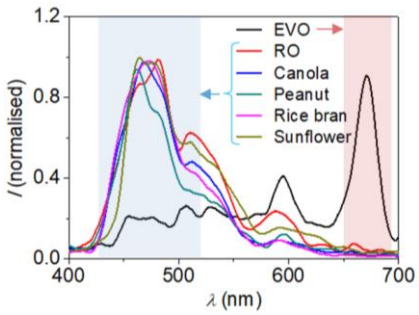


Fig. 3. Emission spectra of vegetable oils of different types measured on the mobile spectrofluorimeter [2].

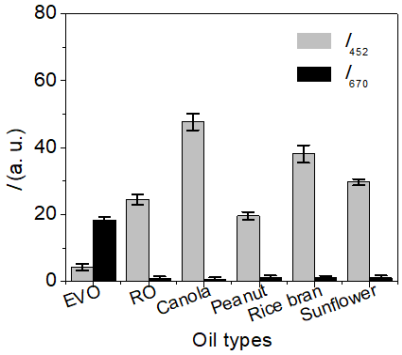


Fig. 4. Comparisons of the emission intensities measured atλ ~ (452 ± 40) nm and λ ~ (670 ± 20) nm bands.

C. *The impact of storage*

The unique characteristics of a particular oil type depends on a number of influences including olive type, cultivation process, olive growth, pressing method and storage conditions [20]. Among them, we have analysed the effects of storage condition using the mobile spectrofluorimeter. To do this, EVO and RO were stored for 30 days under a similar condition of normal supermarket storage; temperature: 22 °C, humidity: 50% and illumination: ~ 400 lux (typical fluorescent light illumination at height ~ 3 m). Spectra of fresh and stored oils are compared in Fig. 5(a) and 5(b). The changes of I_{452} and I_{670} are compared in Fig. 5(c). The storage condition makes a ~ 4.5-fold quenching of EVO fluorescence whereas the changes observed in RO is much lower and found within the experimental error limit. Although no noticeable variation is spotted on the visual appearance, the Chl-*a* emission in EVO spectrum disappears and a weak greenish-blue emission exists. By monitoring the intensity at λ ~ 670 nm, and further quantifying on the app, the user can realise the storing time and extent of degradation of the EVO oil. The degradation of olive oil during storage is primarily attributed to the oxidation by light and heat [48].

D. *Photo-degradation*

The exposure of light to EVO is primarily attributed as the main source of oxidation that makes the degradation oil quality [51]. Due to the presence of the Chl pigments in EVO, the photo-oxidation happens to it more likely than the RO oil. The Chl-*a* molecule in EVO alter their anti-oxidising property in the presence of light and enhances the formation of oxygen radicals. These radicals eventually accelerate oxidation of oil. Chl pigments in EVO are also likely to be deteriorated by demetalation – a light-induced process that produces colourless molecules in the oil. To avoid the photo-degradation that deteriorates the oil's quality, it is desirable to store and sell them in bottle or container that blocks the penetration of light. However, some of them can be seen in market to be sold in optically transparent bottles or containers. To analyse the effect container's transparency on overall photo-degradation, we measured the fluorescence intensity for oils storing in bottles of three different opacities (dark, semi-dark and clear) for the duration of 1 month. Although there is no visual distinction appeared between the samples, a significant change in overall emission particularly at the Chl band (λ_{peak} ~ 670 nm) is recorded in mobile fluorimeter measurements (Fig. 5(d)).The olive oil stored in a completely dark bottle gives strongest red emission, indicating the preservation of its anti-oxidant compounds. In contrast to this, oil stored in transparent bottle shows very weak emission of greenish-blue and the red emission diminished to nearly zero. This proves the direct relationships of photo-degradation of EVO oil on the optical transparency of containers.

Deleted: 9

Deleted:

Deleted: (I_{670})

Deleted:

Formatted: Highlight

Moved up [7]: By analysing the dominating emission bands at λ ~ (452 ± 40) nm and λ_{em} ~ (670 ± 20) nm, different values of intensities, I_{452} and I_{670} are calculated for each oil sample and the results are compared in Fig. 4. The smart app algorithm compares I_{452} and I_{670} to determine the type and status of the oil.¶

Deleted: primarily attributed due to the oxidisation by light and heat…

Deleted: 30

Formatted: Highlight

Deleted: is

Deleted: 32

Deleted: Chl

Formatted: Highlight

Deleted: is

Formatted: Highlight

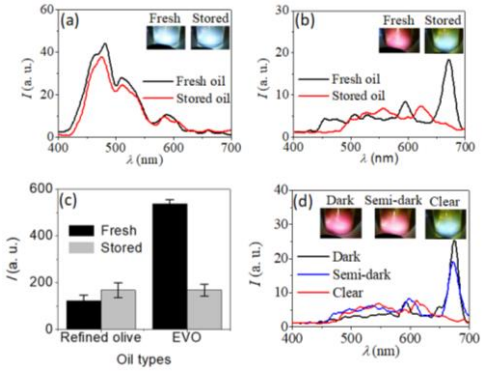


Fig. 5. Storage effect on emission spectra of olive oils measured using the mobile fluorimeter. (a) RO; and (b) EVO oils; and (c) a comparison of intensities measured under the $\lambda \sim 670$ nm band. (d) Emission spectra of EVO oils stored in bottles of three different opacities. Images in insets (a, b, and d) show oil samples under 370 nm excitation [2].

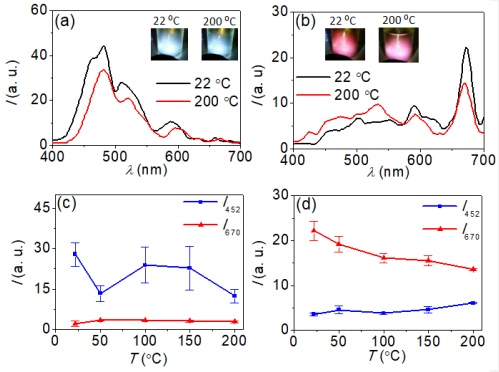


Fig. 6. Thermal effect on olive oils emission – (a) RO and (b) EVO oils measured using the mobile fluorimeter. Relative intensity changes at $\lambda \sim (452 \pm 40)$ nm and $\lambda \sim (670 \pm 20)$ nm bands with rising T in - (c) RO and (d) EVO oils [2].

E. Thermal degradation

In addition to photo-degradation, heat exposure is also considered to be an important factor degrading olive oils and turning them rancid [48], [50]. This is mainly due to the decrease of hydroxytyrosol molecules with rising temperature. Regular use of degraded oils of any types (due to old storage or overheated) may adversely affect the human body. To study the thermal degradation, olive oil samples were heated for different temperatures between $T \sim 22$ and 200 °C and their emission spectra were measured using the smart mobile fluorimeter. The samples are allowed to cool down before each measurement and a dark room ensures no photo-degradation of samples.

Spectra of both EVO and RO oils heated at 22 °C (room temperature) and 200 °C are shown in Fig 6(a) and 6(b). Fluorescence intensities of RO and EVO at $\lambda \sim 452$ and 670 nm are plotted over the T range in Fig. 6(c) and 6(d) respectively. From the thermal analysis, the refined oil is found more stable than the extra virgin olive as expected. Within the experimental error range the results are consistent with those obtained from a benchtop fluorimeter [19]. The fluorescence emissions in EVO sample corresponding to oxidizing and anti-oxidising bands respectively decrease and increase at the rate of $(dI/dT)_{452} \sim 0.50$ and $(dI/dT)_{452} \sim 0.40$. The changes of emission can be ascribed due to the production of oxidation compounds [19].

V. Conclusion

In conclusion, a hand-held smartphone spectrometer with an optical fibre endoscope is demonstrated to be an effective means of differentiating and assessing the quality of EVO and RO oils. We have found an inherent fluorescent marker within EVOs to distinguish them from other vegetable oils. The strong fluorescence bands characteristic of oxidising components present within the more refined oils are observed compared to the EVO oils. Significant changes in oil quality under light and heat can be identified by measuring their fluorescence spectra. Rather than being fake products many EVOs are almost certainly degraded due to their sale within optically transparent bottles. Therefore, it is crucial during bottling, packaging, transportation and storage to limit the exposure of the EVO to light and changes in temperature to ensure that the initial high quality bottled oil reaches the consumer in these same conditions. These types of measurements are essential for rapid field diagnostics and regional mapping [34] during processing, storing and marketing, making interactive customer service and assurance one step closer to fruition.

This work has demonstrated the power of the smartphone spectrofluorimeter – a prominent example of the lab-in-a-phone technology – as a simple, relatively low-cost diagnostic tool at all stages of oil production, transport and retail. This data can be generated and captured live to market via on-line cloud services making it amenable for the international supply of goods directly from the farm to consumer without the need for costly and often prohibitively expensive middle parties.

Acknowledgments

Authors acknowledge Dr. Sandra Ast, at the Australian Sensing and Identification Systems Pty. Ltd. for a technical discussion and suggestion on chlorophyll fluorescence. M. A. Hossain acknowledges an Endeavour Research Fellowship under the supervision of Prof. Abbas Jamalipour at The University of

Formatted: Highlight
Deleted: the
Deleted: attributed
Deleted: as an
Deleted: of degradation
Deleted: of
Formatted: Highlight
Deleted: s
Deleted: into
Formatted: Highlight
Deleted: 31
Formatted: Highlight
Deleted: -
Deleted: 33
Formatted: Highlight
Deleted: reduction
Deleted: rise
Formatted: Highlight
Deleted: on
Deleted: analyse
Formatted: Highlight
Formatted: Highlight
Deleted: 8
Deleted: 8
Deleted: , something that is extremely important for ensuring the economic survival and value of Australian agricultural produce in the future. By ensuring auto-archiving, some level of security can be implemented to enable a global standardization and accountability of product claim and delivery.
Deleted: This technology will strengthen the creation of and confidence in genuine online market places.

Sydney supported by the Australian Government Department of Education and Training. Z. Yu acknowledges a summer scholarship at the *i*nterdisciplinary Photonics Laboratories.

REFERENCES

[1] J. Canning, "Smart devices and photonics for sensing and diagnostics", Emerging Sensing Technologies Summit (ESTS), Melbourne Australia (2016)

[2] A. Jamalipour and M. A. Hossain, "Smartphone instrumentations for public health safety" pp. 1-98, Springer Nature, Switzerland, 2019.

[3] J. Moore, J. Spink, and M. Lipkus, "Development and application of a database of food ingredient fraud and economically motivated adulteration from 1980 to 2010," *J. Food Sci.*, Vol. 77, Issue. 4, pp. R118–R126, Apr. 2012.

[4] E. Waterman and B. Lockwood "Active components and clinical applications of olive oil," *Alternative Med. Rev.*, Vol. 12, Issue 4, pp. 331–342, Dec. 2007.

[5] T. Psaltopoulou, A. Naska, P. Orfanos, D. Trichopoulos, T. Mountokalakis, and A. Trichopoulou "Olive oil, the Mediterranean diet, and arterial blood pressure: the Greek European prospective investigation into cancer and nutrition (EPIC) study," *Am. J.Clin.Nutr.*, Vol. 80, Issue 4, 1012–1018, Oct. 2004.

[6] F. B. Hu "The Mediterranean diet and mortality — olive oil and beyond," *N. Engl. J. Med.*,Vol. 348, Issue 26, pp. 2595–2596, Jun. 2003.

[7] M. T. Morales and R. Przybylski "Olive oil oxidation," in Chapter 13 of *Handbook of Olive Oil* edited by J. Harwood and R. Aparicio, pp. 459-490, Springer Science+Business Media, New York, 2000.

[8] J. N. Soto, S. S. Martínez, D. M. Gila, J. G. Ortega and J. G. García "Fast and reliable determination of virgin olive oil quality by fruit inspection using computer vision," Sensors, Vol. 18, Issue 11, p. 3826, Nov. 2018.

[9] A. I. Martynenko, "Porosity evaluation of ginseng roots from real-time imaging and mass measurements," Food Bioprocess Technol., Vol. 4, Issue 3, pp. 417–428, Apr. 2011.

[10] D. -W. Sun, "Hyperspectral imaging for food quality analysis and control," pp. 496. Academic Press. London: Elsevier Science 2010.

[11] H. Huang, L. Liu and M. O. Ngadi. "Recent developments in hyperspectral imaging for assessment of food quality and safety," Sensors, Vol. 14, Issue 4, pp. 7248-7276, Apr. 2014.

[12] H. Itoh, S. Kanda, H. Matsuura, K. Sakai and A. Sasao. "Measurement of nitrate concentration distribution in vegetables by near-infrared hyperspectral imaging." Environment Control in Biology," Vol. 48, Issue 2, pp. 37-49, Oct. 2010.

[13] A. Zdunek, "Application of Acoustic Emission for Quality Evaluation of Fruits and Vegetables," Chapter 8, pp. 175-208, INTECH Open Access Publisher: Rijeka, Croatia, 2013.

[14] A. J. Rostocki, R. Tarakowski, P. Kiełczyński, M. Szalewski, A. Balcerzak, and S. Ptasznik "The ultrasonic investigation of phase transition in olive oil up to 0.7 GPa," J Am Oil Chem Soc, Vol. 90, Issue 6, pp. 813–818, Mar. 2013.

[15] M. Karaliūnas, K. E. Nasser, A. Urbanowicz, I. Kašalynas, D. Bražinskienė, S. Asadauskas and G. Valušis "Non-destructive inspection of food and technical oils by terahertz spectroscopy," Scientific Reports, Vol 8, Issue Article number: 18025, Dec. 2018.

[16] A. Rohman "Infrared spectroscopy for quantitative analysis and oil parameters of olive oil and virgin coconut oil: A review," Int J Food Properties, Vol. 20, No. 7, 1447–1456, Nov. 2017.

[17] A. G. Mignani, L. Ciaccheri, H. Ottevaere, H. Thienpont, L. Conte, M. Marega, A. Cichelli, C. Attilio, and A. Cimato, "Visible and near-infrared absorption spectroscopy by an integrating sphere and optical fibers for quantifying and discriminating the adulteration of extra virgin olive oil from Tuscany," Anal Bioanal Chem, Vol 399, Issue 3, pp. 1315–1324, Jan. 2011.

[18] B. Gordillo, L. Ciaccheri, A. G. Mignani, M. L. Gonzalez-Miret, and F. J. Heredia "Influence of turbidity grade on color and appearance of virgin olive oil," J Am Oil Chem Soc, Vol. 88, Issue 9, pp. 1317–1327, Sep. 2011.

[19] Y. Gilbert, M. Kongbonga, H. Ghalila, M. B. Onana, Y. Majdi, Z. B. Lakhdar, H. Mezlini, and S. S. Ghalila "Characterization of vegetable oils by fluorescence spectroscopy," *Food and Nutr. Sci.*, Vol. 2, Issue 7, pp. 692–699, Sep. 2011.

[20] E. Guzmán, V. Baeten, J. A. F. Pierna, J. A. García-Mesa, "Evaluation of the overall quality of olive oil using fluorescence spectroscopy," *Food Chemistry*, Vol. 173, pp 927-934, Apr. 2015.

[21] G. Tomazzoni, M. Meira, C. M. Quintella, G. F. Zagonel, B. J. Costa, P. R. de Oliveira, I. M. Pepe, and P. R. da C. Neto, "Identification of vegetable oil or biodiesel added to diesel using fluorescence spectroscopy and principal component analysis," *J. Am. Oil Chem. Soc.*, Vol. 91, Issue 2, 215–227, Feb. 2014.

[22] A. G. Mignani, L. Ciaccheri, A. A. Mencaglia, A. Cimato, "Optical absorption spectroscopy for quality assessment of extra virgin olive oil: in Chapter 3 of "Olive oil - constituents, quality, health properties and bioconversions" edited by B. Dimitrio, *InTech Publisher*, Croatia, pp. 47–62, Feb. 2012.

[23] M. Mowatt "Counterfeit detection in olive oil" *Ocean Optics Newsletters*, May 20, 2015.

[24] A. L. Glantz "Fluorescence of olive oil under ultra-violet light," *Indus. & Eng. Chem. Anal. Ed*, Vol. 2, Issue 3, pp. 256-258, 1930.

[25] C. Cucci, A. G. Mignani, C. Dall'Asta, R. Pela and A. Dossena "A portable fluorometer for the rapid screening of M1 aflatoxin," *Sens. Actuators B: Chem.*,Vol. 126, pp. 467–472, Apr. 2007.

[26] J. Canning "Smartphone spectrometers and other instrumentation," *SPIE Newsroom*, Jan. 2016.

[27]

[28]

[29]

[30]

[31] D. L. Neill, Y. -C. Chang, W. Chen, L. Li, M. Xian, "A smartphone based device for the detection of sulfane sulfurs in biological systems," *Sens. Actuators B: Chem.* Vol. 292, pp. 263-269, Aug. 2019.

[32] M. A. Hossain, J. Canning, Z. Yu, S. Ast, P. J. Rutledge, J. K-H. Wong, A. Jamalipour, and M. J.Crossley "Time-resolved and temperature tuneable measurements of fluorescent intensity using a smartphone fluorimeter," *Analyst*, Vol. 142, Issue 11, pp. 1953–1961, Jun. 2017.

[33] I. Hernández-Neuta, F. Neumann, J. Brightmeyer, T. Ba Tis, N. Madaboosi, Q. Wei, A. Ozcan, M. Nilsson "Smartphone-based clinical diagnostics: towards democratization of evidence-based health care," *J. Internal Medicine*, Vol. 285, Issue 1, pp. 19-39, Jan. 2019.

[34] G. K. Özdemir, A. Bayram, V. Kılıç, N. Horzum, and M. E. Solmaz "Smartphone-based detection of dyes in water for environmental sustainability," *Anal. Methods*, Vol. 9, Issue 4, pp. 579–585, Jan. 2017.

[35] S. K. Vashist and J. H. T. Luong, "Smartphone-based point-of-care technologies for mobile healthcare". *In: Point-of-Care Technologies Enabling Next-Generation Healthcare Monitoring and Management*. Springer, Cham, pp. 27-79, 2019.

[36] M. Zarei "Infectious pathogens meet point-of-care diagnostics," *Biosen. Bioelectronics*, Vol. 106, pp. 193-203, May 2018.

[37] Z. Iqbal and R. B. Bjorklund, "Assessment of a mobile phone for use as a spectroscopic analytical tool for foods and beverages," *Int. J. Food. Sci. & Tech.*, Vol. 46, Issue 11, pp. 2428–243, Nov. 2011.

[38] Y. Intaravanne, S. Sumriddetchkajorn, J. Nukeaw, "Cell phone-based two-dimensional spectral analysis for banana ripeness estimation" Sen. Actuat. B: Chem, Vol. 168, Issue 1, pp. 390–394, 2012.

[39] V. Oncescu, D. O'Dell, and D. Erickson, "Smartphone based health accessory for colorimetric detection of biomarkers in sweet and saliva," Lab Chip, Vol. 13, Issue 16, pp. 3232-38, Aug. 2013.

[40] T. S. Park, C. Baynes, S.-I. Cho and J. -Y. Yoon, "Paper microfluidics for red wine tasting," RSC Adv., Vol. 4, Issue 46, pp. 24356-62, May 2014.

[41] T. S. Park and J. -Y. Yoon "Smartphone detection of escherichia coli from field water samples on paper microfluidics," IEEE Sens. J, Vol. 15, No. 3, pp. 1902-1907, Mar. 2015.

[42] L. J. Loh, G. C. Bandara, G. L. Weber, and V. T. Remcho "Detection of water contamination from hydraulic fracturing wastewater: a μPAD for bromide analysis in natural waters," Analyst, Vol. 140, Issue 16, pp. 5501-7, Aug. 2015.

[43] K. Yang, H. P. -Soroka, Y. Liu, and F. Lin, "Novel developments in mobile sensing based on the integration of microfluidic devices and smartphones," *Lab Chip*, Vol. 16, Issue 6, pp. 943-958, Mar. 2016

[44] M. Á. G. Tamayo, F. E. H. Velasco, J. E. Candelo-Becerra, "Characterization of excitation source LEDs and sensors without filters for measuring fluorescence in fluorescein and green leaf extract," *Telkomnika* . Vol. 17, Issue 4, pp. 1838-1844. Aug. 2019.

[45] M. A. Hossain, J. Canning, S. Ast, P. Rutledge, T. L. Yen, and A. Jamalipour, "Lab-in-a-phone: Smartphone-based portable fluorometer for pH measurements of environmental water," *IEEE Sensors J.*, 15(9), pp. 5095-5102, Sep. 2015.

[46] J. Lapointe, M. Gagné, M. J. Li, and R. Kashyap, "Making smart phones smarter with photonics," *Opt. Express*, Vol. 22, Issue. 1330, 15473-15484, Jun. 2014.

Moved (insertion) [4]

Moved (insertion) [5]

Formatted: Font: Italic

Moved (insertion) [3]

Formatted: Highlight

Formatted: Font: Italic, Highlight

Formatted: Highlight

Deleted: <#> Tomazzoni, M. Meira, C. M. Quintella, G. F. Zagonel, B. J. Costa, P. R. D. Oliveira, I. M. Pepe, P. R. D. C. Neto, "Identification of vegetable oil or biodiesel added to diesel using fluorescence spectroscopy and principal component analysis," *J. Am. Oil Chem. Soc.*, Vol. 91, Issue 2, 215–227, Feb. 2014.¶

Moved up [5]: <#>M. Mowatt "Counterfeit detection in olive oil" Ocean Optics Newsletters, May 20, 2015.¶

Moved up [3]: A. L. Glantz "Fluorescence of olive oil under ultra-violet light," *Indus. & Eng. Chem. Anal. Ed*, Vol. 2, Issue 3, pp. 256-258, 1930. ¶
Tomazzoni, M. Meira, C. M. Quintella, G. F. Zagonel, B. J. Costa, P. R. D. Oliveira, I. M. Pepe, P. R. D. C. Neto, "Identification of vegetable oil or biodiesel added to diesel using fluorescence spectroscopy and principal component analysis," *J. Am. Oil Chem. Soc.*, Vol. 91, Issue 2, 215–227, Feb. 2014.¶

Moved up [4]: A. G. Mignani, L. Ciaccheri, A. A. Mencaglia, A. Cimato, "Optical absorption spectroscopy for quality assessment of extra virgin olive oil: in Chapter 3 of "Olive oil - constituents, quality, health properties and bioconversions" edited by B. Dimitrio, *InTech Publisher*, Croatia, pp. 47–62, Feb. 2012.¶

Deleted: <#>C. Cucci, A. G. Mignani, C. Dall'Asta, R. Pela and A. Dossena "A portable fluorometer for the rapid screening of M1 aflatoxin," *Sens. Actuators B: Chem.*,Vol. 126, pp. 467–472, Apr. 2007. ¶

Formatted: Highlight

Formatted: Font: Italic, Highlight

Formatted: Highlight

Formatted: Highlight

Formatted: Highlight

Formatted: Highlight

Formatted: Highlight

Formatted: Highlight

Formatted: Highlight

Formatted: Highlight

[47] M. A. Hossain, J. Canning, S. Ast, K. Cook, P. J. Rutledge and A. Jamalipour, "Combined 'dual' absorption and fluorescence smartphone spectrometers," *Opt. Lett*. 40, 1737–1740, (2015).
[48] M. A. Hossain, J. Canning, K. Cook and A. Jamalipour, "Optical fibre smartphone spectrometer," *Opt. Lett*. 41(10), 2237-2240 (2016).
[49] J. Lapointe, F. Parent, E. Soares D. L. Filho, S. Loranger, and R. Kashyap "Toward the integration of optical sensors in smartphone screens using femtosecond laser writing," *Optics Letters*, Vol. 40, Issue 23, pp. 5654–5657, Dec. 2015.
[50] Flir Systems "Thermal imaging camera attachment for iOS and Android," FLIR ONE, [Online]. Available: http://www.flir.ca/flirone/. (Accessed on 23 Jul. 2019)
[51] M. Naqshbandi, J. Canning, B. C. Gibson, M. M. Nash, and M. J. Crossley "Room temperature self-assembly of mixed nanoparticles into photonic structures," *Nat. Comm.*, Vol. 3, 1188, Nov. 2012.
[52] R. Cheikhousman, M. Zude, D. J. R. Bouveresse, C. L. Leger, D. N. Rutledge, and I. B. Aragon, "Fluorescence spectroscopy for monitoring deterioration of extra virgin olive oil during heating," *Anal. Bioanal. Chem.*, Vol. 382, Issue 6, pp. 1438–1443, Jul. 2005.
[53] "Health and Olive Oil," The Olive Oil Source, CA, USA. [Online]. Available: http://www.oliveoilsource.com/page/health-and-olive-oil. (Accessed on 23 Jul. 2019)
[54]
[55] M. Zandomeneghi, L. Carbonaro, and C. Caffarata "Fluorescence of vegetable oils: olive oils," *J. Agric. Food Chem*., Vol. 53, Issue 3, pp. 759-766, Feb. 2005.
[56] J. Ayton, R. J. Mailer and K. Graham, "The effect of storage conditions on extra virgin olive oil quality," in RIRDC Publication No. 12/024, *Rural Industries Research and Development Corporation*, Apr. 2012.
[57] M. A. Hossain, J. Canning, S. Ast, P. J. Rutledge, and A. Jamalipour "Early warning smartphone diagnostics for water security and analysis using real-time pH mapping," Phot. Sensors, Vol. 5, Issue 4, pp. 289-297, Dec. 2015.
[58] M. A. Hossain, J. Canning, K. Cook, S. Ast, and A. Jamalipour, "Photo- and thermal degradation of olive oil measured using an optical fibre smartphone spectrofluorimeter", *25th Optical Fiber Sensors Conference*, Jeju, S. Korea, Apr. 2017.

Moved (insertion) [6]

Moved up [6]: R. Cheikhousman, M. Zude, D. J. R. Bouveresse, C. L. Leger, D. N. Rutledge, and I. B. Aragon, "Fluorescence spectroscopy for monitoring deterioration of extra virgin olive oil during heating," *Anal. Bioanal. Chem.*, Vol. 382, Issue 6, pp. 1438–1443, Jul. 2005.¶