



HAL
open science

Measurements of the chromatic refractive index signature of wine models using a fibre long period gratings

T. Allsop, A. Ioannou, K. Kalli, R. S. Bhamber, E. Aguera, A. Samson, Peggy Rigou, Cédric Saucier, Bernard Dussardier

► To cite this version:

T. Allsop, A. Ioannou, K. Kalli, R. S. Bhamber, E. Aguera, et al.. Measurements of the chromatic refractive index signature of wine models using a fibre long period gratings. Optical Sensing and Detection VIII - SPIE Photonics Europe 2024, Apr 2024, Strasbourg, France. pp.1299902, 10.1117/12.3022049 . hal-04792939

HAL Id: hal-04792939

<https://hal.science/hal-04792939v1>

Submitted on 26 Nov 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Measurements of the chromatic refractive index signature of wine models using a fibre long period gratings.

T. Allsop^{a,*}, A. Ioannou^b, K. Kalli^b, R. S. Bhamber^c, E. Aguera^d, A. Samson^d, P. Rigou^e, C. Saucier^e, B. Dussardier^{f,*}.

^a Aston Institute of Photonic Technologies, Aston University, Aston Triangle, Birmingham, B47ET, UK; ^b Cyprus University of Technology, PhOSLab, Limassol, 3036, Cyprus; ^c Department of Population Health Sciences, Bristol Medical School, University of Bristol, UK; ^d INRAE, UE999 Pech Rouge, 11430 Gruissan, France; ^e SPO, Université de Montpellier, INRAE, Institut Agro, 34000 Montpellier, France; ^f Université Côte d'Azur, CNRS, Institut de Physique de Nice (INPHYNI), Nice, France

corresponding authors: t.d.p.allsop@aston.ac.uk & bernard.dussardier@univ-cotedazur.fr

ABSTRACT

A novel optical fibre device is proposed for real-time measurements of near infrared chromatic refractive index signature of a liquid medium in the 1100-1700 nm range. This inline optical fibre chromatic refractive index analyser is based upon collocated fibre long period gratings written adjacently in the core by femtosecond laser inscription yielding 8 attenuation bands associated with different cladding modes, yielding 8 independent measurements across the entire wavelength range. This fibre device is tested on a series of chemical compounds associated with wines. The results for each compound yielded distinctive chromatic responses. The limits of detection for this fibre devices ranged from 1×10^{-3} to 6×10^{-5} mol/L for the compounds associated with wines. This demonstrates a potential usefulness of such an optical fibre sensor capable of monitoring in real-time effective chromatic refractive index signatures that is not offered by any current technology.

Keywords: optical fibre sensor, refractive index, chromatic dispersion, long period gratings, real-time monitoring, wine fingerprinting and traceability

1. INTRODUCTION

Long period gratings (LPGs) inscribed in optical fibres have been routinely used to measure the changes in refractive index (RI) of countless liquids surrounding the bare cladding of the fibre, by monitoring the wavelength shift and amplitude changes in one attenuation bands of the transmission spectrum. This has been realized using a number of configurations over the last couple of decades, from simple uniform LPGs to specific thin-film coated LPGs to yield index changes with chemical specificity^{1,2}. LPG refractive index modifications typically have periods ranging from 100 to 500 μm . They behave as a dispersive optical element, that couples core guided modes and guided cladding modes. This results in deep notches in the wavelength-based transmission spectrum of an optical fibre that contains the said LPG, and the global transmission spectrum is characterised by several attenuation bands³. LPGs are therefore an attractive form of optical fibre sensor, due to an inherent sensitivity to strain, temperature, RI, bending and load/compression^{4,5,6}. The central wavelength λ_v of an attenuation band is specified by the phase-matching condition:

$$\delta n_{effv} \cdot \Lambda = \lambda_v \quad (1)$$

where $\delta n_{effv} = [n_{co}^{01}(\lambda, \varepsilon, T, R, n_1, n_2) - n_{cl}^{1v}(\lambda, \varepsilon, T, R, n_1, n_2, n_s)]$, where n_{co}^{01} is the effective index of the core mode, n_{cl}^{1v} the effective index of the v^{th} radial cladding mode, with both indices identifying the cladding mode order and a dependence on the refractive index and the optical fibre geometry, n_1 is the refractive index of the core, and n_2 the refractive index of the cladding and the wavelength λ . Moreover, n_{cl}^{1v} is a function of the RI of the surrounding medium, n_s . Λ is the LPG period, T the temperature and ε the strain (compression in this situation) experienced by the fibre along with R the curvature³. The quantity δn_{effv} is defined as the differential effective index between the core and cladding modes. The superscripts with respect to the core mode denote the LP₀₁ mode and in the case of the cladding modes refers to the HE_{1v} axially symmetric cladding modes. As the grating is assumed to have a circular symmetry, the only non-zero coupling coefficients between the core mode and the cladding modes involve cladding modes of azimuthal order 1.⁷

There are other configurations of fibre devices based on LPG technology that utilize the material and waveguide dispersive properties of the optical fibre to produce dual-peak attenuation band resonance. This occurs where the phase-matching of the cladding mode to the core mode is at a dispersion turning point of the optical fibre⁸. These strategies have been employed to measure the RI of the surrounding medium at one or over a very small wavelength range, in fact over a few nanometers⁹. However, LPGs usually have several attenuations over a very much larger spectral range, therefore they can be used to estimate the chromatic RI properties of the medium into which they are submerged. Implementing specially developed LPG such a way would have a great advantage, as compared to usual ellipsometry technics in free space configuration.

For the first time, to the authors' knowledge, we use a series of attenuation bands from a LPG double structure inscribed into a singlemode fibre (Bi-LPG) to simultaneously measure the RI of a liquid at different wavelengths. The femtosecond inscribed LPG is designed to couple the core mode to different centro symmetric cladding modes associated with each attenuation band¹⁰, to yield independent measurements, to arrive at the chromatic RI curve of the material in the near infrared spectral region. The first "full potential" implementation of the Bi-LPG fibre device concept is achieved by multiplexing several independent measurements at the same spatial location, simultaneously. To test the potential of the Bi-LPG device to do sampled measurements of RI chromatic signatures, we considered an interesting real-world application, that is the detection versus concentration, in solution, of chemical compounds found in commercial drinks, such as wine, to determine the limit of detection (LOD) of the said compounds.

2. EXPERIMENTAL AND METHOD

Fibre device fabrication and characterization

The Bi-LPG structure consists of two LPGs written adjacent to each other (side by side) in the core of a type G.652 single mode fibre, using a femtosecond laser inscription scheme, with periods of 339 and 525 μm , respectively, and 50/50 duty cycle. The LPG lengths are 31.866 and 26.26 mm long, respectively. The LPGs have been annealed after laser inscription. The Bi-LPG fibre was positioned in a flat metallic V-groove, placed on a granite optical table, which acted as a heat sink to help maintain a constant temperature throughout the experiments. Their transmission was calibrated in function of temperature and RI using calibrated index fluids (Cargille Labs) that have a quoted accuracy of ± 0.0002 . The transmitted spectrum from a fibre connected tungsten lamp (Ando AQ4305) across the Bi-LPG fibre was collected by an optical spectrum analyser (OSA, Yokogawa, AQ6370D, minimal resolution 0.05 nm). This Bi-LPG yields 9 attenuation bands from 1134 to 1644 nm (Figure 1). All bands, except the 2nd, had a monotonic wavelength shift vs. RI. Therefore, in the following, the device was characterized and used using 8 attenuation bands.

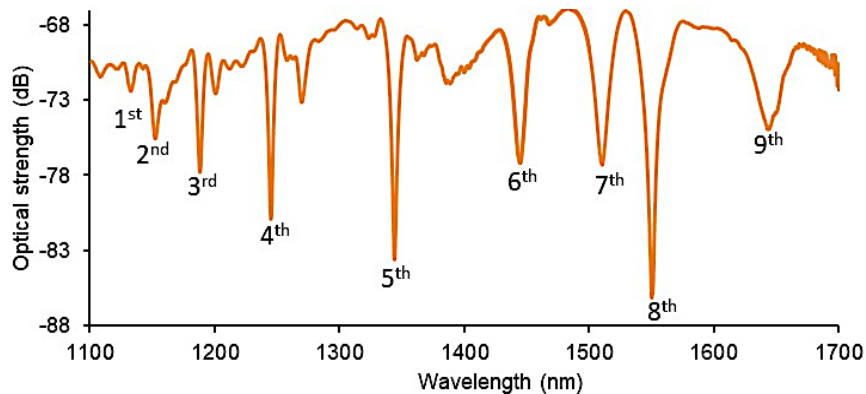


Figure 1. The transmission spectrum of the Bi-LPG sensors with periods of 339 μm and 525 μm , for a 50 % duty cycle in air and at a temperature of 23.5 $^{\circ}\text{C}$.

A 0.2-ml drop of a liquid, or solution containing a specific compound (see below), was set on the Bi-LPG, and the wavelength shift of each attenuation band was recorded vs. the compound concentration in this solution. Between two measurements, the Bi-LPG was rinsed in ethanol until all bands had recovered their initial spectral location, both in ethanol and in air. The temperature was measured at a precision of 0.1 $^{\circ}\text{C}$ to correct the transmitted spectra from temperature slow drifts. The central wavelengths of each band was its centroid calculated by geometric decomposition¹¹. Ultimately,

the minimal detectable wavelength shift was 6 pm, limited by the OSA and the number of data points per scan. The associated error was estimated thanks to a stability measurement : the transmission spectra of the Bi-LPG sensors were taken over a 40 mins intervals? The observed spectral noise had a standard deviation of $\Delta\lambda_{\text{error}} = 16$ pm in wavelength and 2.2 m dB errors in intensity, associated with the centroid measurement approach and measurement resolution of 6 pm. The error was estimated calculating the standard deviation from the measured mean of 3 consecutive measurements for the wavelength and the optical strength combined at the specific wavelength, divided by the root of the number of data points. This yields an error of ± 2 pm. The spectral index sensitivity of the attenuation bands ranges from -117 to +179 nm/RIU with an average of 52 nm/RIU; whereas their temperature sensitivity ranges from ~ 0 to $+0.1$ nm/ $^{\circ}\text{C}$.

Analyte solutions preparation.

The base of all the synthetic solutions was a mixture of pure water, tartaric acid (5 g/L), ethanol (12%), and was adjusted at pH= 3.5 with NaOH. The analytes tested were selected from compounds representative of the main compounds present in wine, with a large typical concentration difference between the most concentrated (such as malic acid) and the least concentrated (such as malvidin). The selected compounds are : malic acid, lactic acid, acetic acid, ethyl-4 phenol acid, methional, sotolon, acetaldehyde, catechin and malvidin. For each compound, a mother solution was sequentially diluted 10 times to span the concentrations on typical ranges 0.001 to 100 g/L (e.g. malic acid) down to 10^{-5} to 1 g/L (e.g. malvidin), on logarithmic scales. For each compound, the mid-range concentrations correspond to the typical content in a large variety of wines, i.e. the lowest concentrations in each series was implemented to test whether the LOD was lower than the expected concentration in a “real” wine.

3. RESULTS

The RI changes in function of the solution concentrations for each compound series are displayed in Figure 2(a). The two important parameters that can be deduced are the resolution, defined as $\Delta\lambda_{\text{error}}/S\lambda_B$, where $S\lambda_B = \Delta\lambda/\Delta n_s$ is the bulk RI sensitivity, and the LOD.

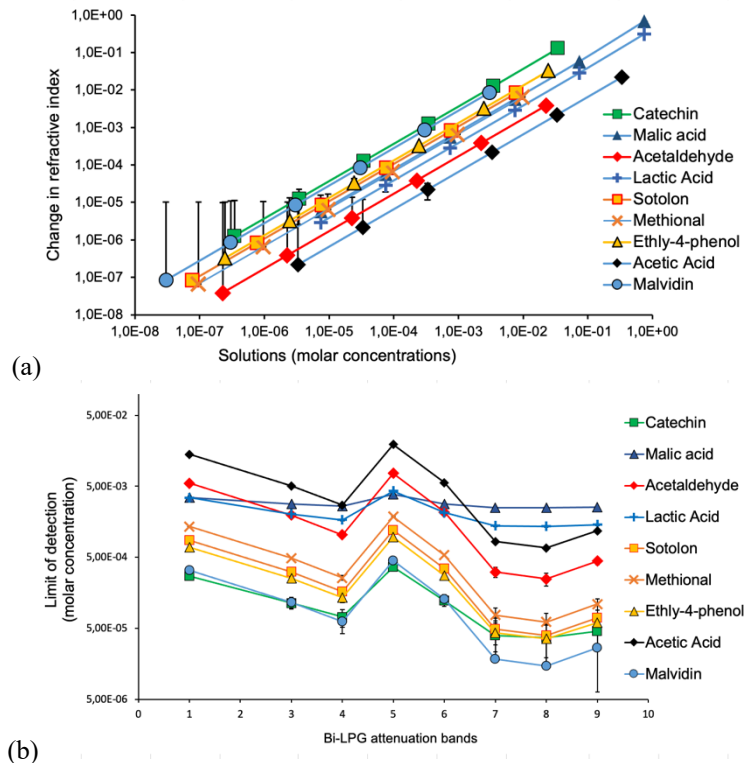


Figure 2(a) The RI as a function of the chemical concentrations (b) the estimated limit of detection of the attenuation bands of the Bi-LPG. All results have been temperature compensated to ensure the observed wavelength shifts are due to RI changes.

The LOD is dependent on the interrogation scheme, the light source spectral width, and the noise bandwidth of the measurement system. It can be expressed in terms of standard deviation of noise of the sensor output $\Delta\lambda_{error}$, the bulk sensitivity $S_{\lambda B}$ and the bandwidth of the spectral transmission feature of the attenuation bands $\Delta\lambda_{feature}$. $\Delta\lambda_{feature}$ is the FWHM of the resonance for each attenuation band (Figure 1). Each band is described by $N = 120$ discrete spectral data points per spectral scan on the OSA across the resonant peak. The limit of detection is expressed as :¹²

$$LOD = \sqrt{(2(\Delta\lambda_{feature} + \Delta\lambda_{error})/N)/S_{\lambda B}} \quad (2)$$

Thus, the individual attenuation band will yield different index resolutions varying from 1.85×10^{-3} RIU to 8.34×10^{-5} RIU. In practice, the LOD are estimated by using polynomial regressions to data points that have gradients with adjacent data with different concentrations and using the $\Delta\lambda_{error}$ at the limit to distinguish individual measurements. The estimated LOD for the compounds used are shown in Figure 2(b) and are consistent with experimental results for the different chemicals. Whilst the smallest changes in RI are shown in Figure 2(a), in practical experiments, the temperature was monitored with an accuracy of 0.1 °C. The smallest RI changes would be dominated by the random variations in temperature of 0.05 °C that would lead to 1.3 pm fluctuations in wavelength, a value that is the equivalent of approximately 3×10^{-5} RIU. Thus, detection of lower concentrations is not possible. Considering the application of Bi-LPG to investigate model wines, it was found that the LOD of almost all compounds is well below the known concentrations found in many wines. The exceptions concern sotolon, ethyl-4 phenol acid and methional, of which the found LOD overlaps the bottom of the expected range in some types of wines where these compounds are in low concentrations.

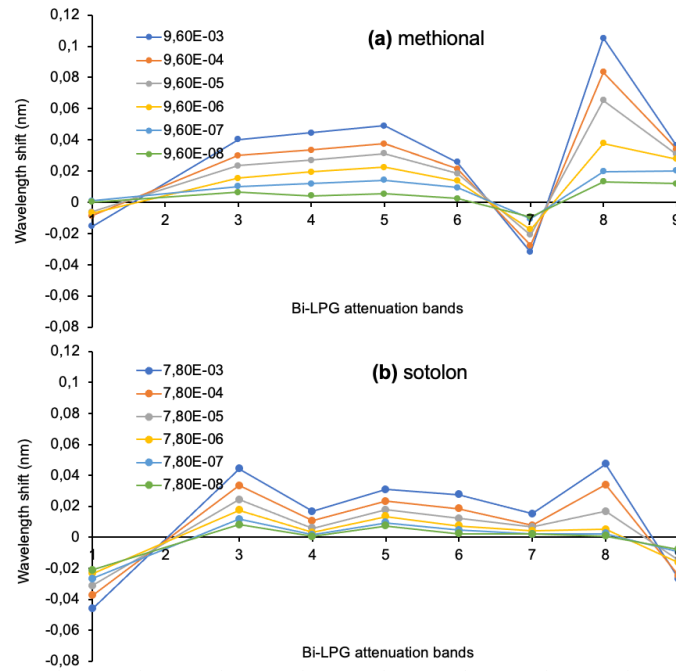


Figure 3: Wavelength shift of the Bi-LPG attenuation bands at various molar concentrations (in the legend: mol/L) of (a) methional and (b) sotolon chemical compounds. Error bars are (± 1.3 pm), size of the markers. The straight lines are guides for the eye.

Two examples of measurements of the wavelength shift across all canals, versus the compound concentration are shown in Figure 3, in the case of low-concentrated compounds, methional and sotolon. In these graphs, the base-line (0-nm shift) corresponds to the signal obtained from the base model wine, i.e. containing none of the compounds studied here. Although the wavelength shifts are small (a few 10s of pm), it is seen that the wavelength shift relationship vs concentration yields distinctively dissimilar chromatic responses between compounds. The data displayed in Figure 3 are typical results; dissimilar chromatic signatures were obtained from the other chemicals used in this investigation. This would suggest that the Bi-LPG fibre device has spectral functionality to potentially identify different chemicals within a given solution via the chromatic RI measurement.

The changes in optical strength of the attenuation bands is not reported here, because these remained reasonably constant throughout the experiments. This is expected due to the small changes in the RI and the lesser optical strength spectral sensitivity.

4. CONCLUSIONS

The flexibility associated with the femtosecond laser inscription allows fabrication of Bi-LPGs with periods that generate the attenuation bands distributed within the spectral range 1100 nm to 1690 nm, with the 1st attenuation band at 1134.4 nm and the 9th one at 1644 nm. Each transmission feature is associated with a different HE_{1ν} cladding mode. This yields independent refractive index (RI) measurements at the same spatial location, producing a sampled measurement of the chromatic RI variations and any associated change with its surroundings.

Excepted for 3 analytes studied, the obtained LOD are below the expected concentrations in most wines. This is an encouraging result. For analytes found at very low concentration in wines (such as the 3 studied: sotolon, ethyl-4 phenol acide and methional), some engineering to improve the LPG and fibre designs is possible. Overall, these results show the potential of such a RI chromatic signature LPG fibre device.

It is not possible to compare such an in-situ device with other sensors because the reported ones only measure at a single wavelength, thus measuring a single refractive index and not chromatic index or dispersion curve of the surrounding medium. Moreover, we have shown that the Bi-LPG device produces individual distinctive chromatic RI curves for a given solution. This offers an additional way to investigate and characterise a complex liquid product as an entity. This first demonstration illustrates the potential usefulness of the Bi-LPG fibre device as a new analytical tool for monitoring in real-time in-line fabrication processes of various products such as wine. Furthermore, this is the first time that the “full near infrared” spectral behaviour of a fibre LPG device has been exploited, that is, multiplexing several independent measurements in the near-infrared spectral range (attenuation bands, associated with different cladding modes) at the same spatial location at the same time.

ACKNOWLEDGEMENTS

This work was partially supported by University of Hull prosperity partnership: EP/R004900/1 from the UK Engineering and Physical Sciences Research Council, by CNRS (Centre National de la Recherche Scientifique (visiting researcher position for T.A. Work contract # 1027296), by INRAE.

REFERENCES

-
- [1] T. Allsop, L. Zhang, I. Bennion, “Detection of organic aromatic compounds in paraffin by a long-period fibre grating optical sensor with optimized sensitivity,” *Opt. Comms.* **191**,181-190 (2001). [[https://doi.org/10.1016/S0030-4018\(01\)01131-2](https://doi.org/10.1016/S0030-4018(01)01131-2)]
 - [2] W. Gan et al., “Rapid and sensitive detection of Staphylococcus aureus by using a long-period fiber grating immunosensor coated with egg yolk antibody,” *Biosens. & Bioelectron.* **199**, 113860 (2022). [<https://doi.org/10.1016/j.bios.2021.113860>]
 - [3] T. Allsop, D. J. Webb, I. Bennion, “A comparison of the sensing characteristics of long period gratings written in three different types of fiber,” *Opt. Fib. Technol.* **9**, 201-223 (2003). [[https://doi.org/10.1016/S1068-5200\(03\)00028-2](https://doi.org/10.1016/S1068-5200(03)00028-2)]
 - [4] A. Vengsarkar et al. “Long-Period Gratings as Band-Rejection Filters,” *J. Light. Technol.*, **14**, 58-64 (1996). [<https://doi.org/10.1109/50.476137>]
 - [5] V. Bhatia, A.M. Vengsarkar, “Optical fibre long-period grating sensors”, *Opt. Lett.* **21**, 692-694(1996). [<https://doi.org/10.1364/OL.21.000692>]
 - [6] H.J. Patrick, A.D. Kersey, F. Bucholtz, “Analysis of the response of long period fibre gratings to external index of refraction”, *J. Light. Technol.* **16**, 1606-1612 (1998). [<https://doi.org/10.1109/50.712243>]
 - [7] T. Erdogan, “Cladding-mode resonances in short- and long-period fibre Grating filters”, *J. Opt. Soc. Am. A.* **4**, 1760-1773 (1997). [<https://doi.org/10.1364/JOSAA.14.001760>]
 - [8] Q. Ling, Z. Gu, K. Gao, “Smart design of a long-period fiber grating refractive index sensor based on dual-peak resonance near the phase-matching turning point”, *Appl. Opt.* **57**, 2697 (2018). [<https://doi.org/10.1364/AO.57.002693>]

-
- [9] J. U. Porep, D. R. Kammerer, R. Carle, “On-line application of near infrared (NIR) spectroscopy in food production”, *Trends in Food Science & Technology* **46**, 211 (2015). [<https://doi.org/10.1016/j.tifs.2015.10.002>]
- [10] D. Viveiros et al. “Spectral Tuning of Long Period Fiber Gratings Fabricated by Femtosecond Laser Micromachining through Thermal Annealing,” *MDPI Proc.* **15**, 4 (2019). [<https://doi.org/10.3390/proceedings2019015004>]
- [11] A.M. Bronstein, M.M. Bronstein, R. Kimmel, *Numerical geometry of non-rigid shapes*. (Springer Science & Business Media, 2008). [<https://doi.org/10.1007/978-0-387-73301-2>]
- [12] R. D’Agata, G. Spoto, “Surface plasmon resonance imaging for nucleic acid detection,” *Anal. Bioanal Chem.* **405**, 573–584 (2013). [<https://doi.org/10.1007/s00216-012-6563-9>]