

## Effect of orange peel in whole oranges' spectra

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### Abstract

Nowadays non-invasive methods are gaining more and more attention by the industry and agriculture because they can be fast, reliable and effective to evaluate fruit quality and maturity. In the literature, one can find robust calibration models based on the Visible-Near Infrared spectroscopy (Vis/NIRS) for various fruits to predict fruit quality and ripening indicators such as soluble solids content (SSC), firmness, titratable acidity (TA), etc. The development of these models requires extensive data analysis of the obtained Vis/NIR spectra and data obtained by the standard quantification methods (total soluble solids and titratable acidity). Moreover, physical damages and/or disorders in fruits can also be investigated with spectroscopy techniques. However, peel thickness of the fruit demonstrates to be a critical aspect when one is using optical spectroscopy. Indeed, when one considers citrus, the thick peel with flavedo and albedo might imply that most of the light may not reach the pulp. In the present study, it was evaluated how orange's (*Citrus sinensis*, cv. 'Valencia late') peel affects the reflectance spectra of Vis/NIRS. The fruit spectra were acquired in total darkness with an interactance probe connected to a spectrometer. Spectra samples were taken from the whole orange, discs of peel and from the pulp. To address the water influence in the peel, relative turgidity was calculated. The obtained results allowed the conclusion that there are significant differences between the spectra, that is, the orange spectra are dominated by peel and may differ clearly from the pulp spectra.

**Keywords:** non-invasive, orange, peel, spectroscopy, reflectance

### Resumo

**Efeito da casca de laranja no espectro do fruto inteiro.** Atualmente os métodos não invasivos merecem cada vez mais atenção por parte da indústria e pela agricultura. Isto deve-se ao fato de serem rápidos, confiáveis e efetivos na avaliação da qualidade e maturidade da fruta. Na literatura pode encontrar-se modelos de calibração robustos que recorrem a espectroscopia do Visível-Infravermelho Próximo (Vis/NIRS) para várias frutas, de modo a prever a sua qualidade e estado de maturação através de correlação dos espectros com sólidos solúveis totais, firmeza, acidez titulável, etc. O desenvolvimento destes modelos requer uma extensiva análise de dados obtidos dos espectros Vis/NIR e dos dados obtidos por métodos clássicos (sólidos solúveis totais e acidez titulável). Além destes parâmetros, também se investiga o diagnóstico de danos físicos e alterações fisiológicas dos frutos. Contudo, a espessura da casca dos frutos apresenta dificuldades ao uso de espectroscopia ótica. No caso das laranjas, a espessa casca composta por flavedo e albedo pode implicar que grande parte da luz não atinja a polpa. Neste trabalho foi avaliado o efeito da casca da laranja (*Citrus sinensis*, cv. 'Valencia late') no espectro Vis/NIR de reflectância do fruto inteiro. Os espectros foram tirados no escuro, com uma fibra de interactância conectada a um espectrómetro. As amostras consistiram em laranjas

inteiras, discos de casca e polpa. Para averiguar a influência da água no espectro da laranja, a turgidez relativa da casca foi determinada. Os resultados obtidos permitem concluir que há diferenças significativas entre os espectros, isto é, nas condições deste trabalho, o espectro da laranja é dominado pela casca e difere claramente do espectro da polpa.

**Palavras-chave:** não-invasivos, laranja; casca, espectroscopia, reflectância

## Introduction

Nowadays the demand of high quality fresh fruit by consumers is increasing worldwide and the industry needs to keep up with this trend. In order to do that, industry is looking for some emerging, non-invasive and more cost-effective technologies to be used as an option to the present standard methods, that are invasive and very time consuming. Non-invasive methods are characterized for being fast, reliable and effective to evaluate fruit quality and maturity (Nicolai et al., 2007). Among these technologies Visible and Near-Infrared spectroscopy (Vis/NIRS) is being applied with success to several fruit (Liu et al., 2015; Magwaza et al., 2012). As in most of the spectroscopic techniques applied to complex biological matrices, this technique also requires multivariate analysis to extract information from the spectra.

One finds in the literature, robust calibration models (validated with traditional methods) developed with the Visible-Near Infrared spectroscopy (Vis/NIRS) for various fruits to predict fruit quality and ripening indicators such as soluble solids content (SSC), firmness and acidity (Cayuela, 2008; Clark et al., 2003; Lammertyn et al., 2001, 1998). Moreover, physical damages and/or disorders in fruits can also be investigated with spectroscopy techniques (Johnson, 1985; Peiris et al., 1998).

However, there are some technical aspects that require more study. One of them is the peel thickness of some fruits, because it appears to be a critical aspect when using optical spectroscopy (Jamshidi et al., 2014; Wang et al., 2016). Wang et al. (2014) found that the penetration depth in NIR spectroscopy is larger than in Vis spectroscopy, with values up to 4 mm, thus carrying more information than visible light.

The thick peel of oranges, constituted by the flavedo and the albedo, is a strong obstacle to the pulp and may scatter and/or absorb most of the infrared light before it reaches the pulp. This raises obvious questions about the evaluation of internal quality parameters, namely, SSC (Fraser et al., 2003; Wang et al., 2016). It is known that the amount of radiation that passes through the fruit is affected by the light scattering properties of the tissues (Peiris et al., 1998). Additionally, after the light enters an orange through the peel it is also needed that the back scattered light intensity is enough for a proper measurement (Peiris et al., 1998). Fraser et al. (2003) reported that for mandarin the peel reflects light back to the pulp in a significant fashion. However, there is indication that could exist a correlation between the SSC in the pulp and in the peel (Wang et al., 2016). In the Vis/NIR range the light propagation in fruit usually obeys the diffusive regime, when the scattering properties, quantified by the reduced scattering coefficient,  $\mu'_s$  (mm<sup>-1</sup>), dominate the absorption properties, quantified by the absorption coefficient,  $\mu_a$  (mm<sup>-1</sup>):  $\mu'_s \gg \mu_a$  (Ishimaru, 1989). For example, Fraser et al. (2003) determined that this was clearly observed in mandarin pulp at 808 nm:  $\mu_a = 0,001 \text{ mm}^{-1}$  and  $\mu'_s = 1 \text{ mm}^{-1}$ .

Like any other fruit, oranges' composition is mainly water. Therefore, one might expect that the spectrum of water could, in theory, explain most of the orange spectrum profile. This line of thought has been explored and the approach followed in this work was to fit to water spectrum to the orange spectrum through the reflectance expression derived from the diffusion approximation (Kienle & Patterson, 1997). Studies in other fruit, for example apples and tomatoes, were conducted previously and the results showed

that indeed water spectrum can explain the most of the fruit spectrum in the Vis/NIR range (Cubeddu et al., 2001; Hale & Querry, 1973).

Aside from water the major components of peel and pulp are volatile oils, pectin, dietary fibers, sugar and acids and sugars (Farnworth et al., 2001).

The objective of this study was to find the similarities and dissimilarities between the spectra of the oranges and those of their single constituents (peel and pulp) by considering the absorption spectrum of water in the framework of diffusion approximation.

## Materials and methods

**Fruit samples and water content.** For this assay a total of ten oranges ‘Valencia late’ were bought in the local supermarket and kept at ambient temperature.

Six discs of peel were carefully cut at the equatorial region of the orange with an in house-built hollow round hole punch tool of diameter approximately 1,9 cm. Three of these went to a dry process at 70 °C during approximately 3.5 h, while the remaining ones were placed inside Petri dishes with abundant demineralized water for approximately 3 h.

For both assays the discs’ mass was measured before and after, which allowed to calculate the water percentage and the relative turgidity (Barrs & Weatherley, 1962).

**Spectrum acquisition.** For the acquisition of whole oranges’ spectra, six previously marked positions on the equatorial region were assessed. The measuring fiber was placed in the normal to the sample surface and the spectra was acquired in the darkness. In the next step the discs were cut and clean with absorbent paper, to avoid water on the peel. The peel disc was then placed on top of a polystyrene sphere with similar size of the oranges. The peeled orange exposed by the extraction of the discs was used to acquire the pulp spectra after carefully remove the loose albedo avoiding damaging the segment of the orange.

The acquisition setup consisted on a CCD spectrometer USB2000+ (Ocean Optics, USA) custom tailored to optimize the response in the NIR region (680 – 1150 nm), a tungsten halogen light source (HL-2000, Ocean Optics, USA), a custom interactance probe (OceanOptics, USA) with six receiving fibers disposed in equidistant positions along a 5 mm radius circle centered on the collecting fiber (600 µm core fibers) and a homemade sample holder. The software SpectraSuite was used to acquired spectra ranging from 680 to 1150 nm. However, the spectra were narrowed to the range of 720 to 1100 nm due to considerable noise. Arbitrary reflectance (in the sense that it is not an absolute reference) was calculated dividing the sample spectrum by the reference which was a reflective standard (WS-1-SL, Ocean Optics, USA).

The water spectrum used for the best fit was a combination the two spectra at different ranges 380-725 nm and 725-2500 nm described by Pope & Fry (1997) and Palmer and Williams (1974), respectively.

**Data analysis.** The determination of the optical coefficients was made by means of fitting the experimental data (orange spectrum) to the expression of spatially resolved reflectance obtained within the framework of diffusion approximation. We have adopted the solution derived by Kienle & Patterson (1997) assuming extrapolated-boundary-conditions and a semi-infinite planar medium:

$$R(\rho) = \frac{1}{4\pi} \left[ z_0 \left( \mu_{eff} + \frac{1}{r_1} \right) * \frac{e^{-\mu_{eff}r_1}}{r_1^2} + (z_0 + 2z_b) \left( \mu_{eff} + \frac{1}{r_2} \right) * \frac{e^{-\mu_{eff}r_2}}{r_2^2} \right] \quad (1)$$

Here  $\mu_{eff} = \sqrt{3\mu_a\mu_t}$  is the effective transport coefficient,  $\mu_t = \mu_a + \mu'_s$  is the total extinction coefficient,  $z_0 = 1/\mu_t$  is the depth of the equivalent point source,

$z_b = 2D(1 + R_{eff})/(1 - R_{eff})$  is a factor introduced by the boundary conditions and related with a negative image source, where  $R_{eff}$  is the fraction of photons that is internally diffused reflected at the boundary and was considered to be 0.493 (Haskell et al., 1994) and  $D = 1/(3 * \mu_t)$  is the diffusion coefficient. Finally,  $r_1 = \sqrt{(z_0^2 + \rho^2)}$  and  $r_2 = \sqrt{((z_0 + 2z_b)^2 + \rho^2)}$  are the distances from the sources to the observation point. Globally, the expression depends fundamentally on the reduced scattering coefficient,  $\mu'_s$  and on the absorption coefficient,  $\mu_a$ . In order to restrict the fitting range for these parameters we have made the assumption that  $\mu_a = \%H_2O * \mu_w$ , where  $\%H_2O$  is the percentage of water derived from the dry mass measurements (**Tables and Figures**

), and  $\mu_w$ , is the absorption spectrum of water. The fit of the spectra to eq. (1) was performed on Matlab (Mathworks, USA). The absorption coefficient was allowed to vary by 10 % around  $\%H_2O * \mu_w$ , to compensate for eventual dry mass determination errors. The reduced scattering coefficient at 700 nm was allowed to vary between 0,1 and 5 mm<sup>-1</sup> and we have also allowed for a dependence on wavelength according to a simple interpretation of scattering through Mie theory (Cubeddu et al., 2001):  $\mu'_s = a\lambda^k$ , with  $k$  taking values between -2 and 0. Hence, a grid of values for all the combinations of  $\mu_a$ ,  $\mu'_s$  and  $k$  and the reflectance spectrum with lower RMS was chosen as the best fit. This is a direct and computationally expensive method, but the computation is anyway very fast due to the relatively low number of points. The range of the spectrum used for this computation was from 912 to 1125 nm, in order to match the local absorption peak of water around 970 nm.

## Results and Discussion

**Whole orange, pulp and peel on sphere spectra.** The results shown that there are some observable differences between the three spectra taken from the same orange, that is whole orange, peel on polystyrene sphere and pulp. A priori one could expect dissimilar spectra, given the known difference between peel and pulp (Farnworth et al., 2001). In **Error! Reference source not found.** results of two oranges are presented. The spectra of orange A (**Error! Reference source not found.** A) demonstrates that the spectrum of a whole orange can be almost identical to that of the isolated peel. Whereas for orange B (**Error! Reference source not found.** B) there are some differences, yet very similar spectra were obtained. This difference could be explained by the possible differences in rugosity of the peel surface or even by some experimental drift. Overall, although these two spectra seem identical in both oranges they are different from the respective spectrum of the pulp.

The main differences between peel and pulp are on the 750 to 900 nm range. There is a first noticeable difference at 720 nm that can be due to the absorbance of chlorophyll 1 at 675 nm (Zude-Sasse et al., 2002). The second difference is that the 800 - 900 nm plateau observed for the oranges is not observed for the pulp. These differences were also reported by Wang et al. (2004) and Jamshidi et al. (2001) and it is associated to the third overtones of the O-H band and C-H at 740 nm and 840 nm, respectively. Additionally, the fourth overtone of C-H can explain the absorbance at 740 nm. For an easy comparison, the spectra were normalized to their respective maximum at 970 nm (**Error! Reference source not found.** C and D). Therefore, these results demonstrate that the orange spectra acquired with this setup is mainly determined by the orange peel, which means that scarce information may be inferred about the pulp and thus about the juice (Wang et al., 2016).

**Water best fit.** The fitting method proposed here assumes that the absorption by the orange tissues is dominated by water in the range ~ 900 to 1100 nm, where it has a

local absorption peak. Direct observation of the reflectance spectra suggests immediately that. The fit implements that approximation by assuming an absorption coefficient proportional to the %H<sub>2</sub>O and to the absorption spectrum of water. The average value for the reduced scattering coefficient is  $1.18 \pm 0.27 \text{ mm}^{-1}$ , which is in good agreement with published results (Fraser et al., 2003). Also, the average value of  $k$ ,  $-0.085 \pm 0.17$ , is within the values known for other fruit (Cubeddu et al., 2001). But how good is this approximation? Two different results obtained through the fits are shown in **Error! Reference source not found.A** and **B**. In this figure one may observe that the fitted spectrum is indeed very close to the experimental one in the 900-1100 nm band. The differences are observable for wavelengths below 900 nm, which is expected because the water absorption drops to very low values in this region, causing other tissue components (such as organic compounds, as already referred above) to dominate the absorption component. As a consequence, the actual reflectance becomes lower than predicted because other components are absorbing more than water does. Thus, the close to the peak of absorption of water the better is the fit, which breaks in regions farther away.

The comparison of **Error! Reference source not found.** and 2 shows that the pulp spectra are much closer to the fitted water spectrum across all wavelength range than the orange and peel spectra (particularly, it is slightly increasing from the NIR to the 700 nm, similarly to the fitted spectra and contrary to the peel and whole orange spectra).

The difference between the fitted spectra and the peel spectra should reflect the influence of other components in the 700-900 nm range and one would expect that the difference profiles would follow similar patterns. Indeed, this was observed in **Error! Reference source not found.C**. Local absorption dips at  $\sim 820 \text{ nm}$  and  $\sim 890 \text{ nm}$  may allow the quantification of some other components. Further study and understanding of the meaning of these difference will be carried in the future.

## Conclusions

This work allowed a better understanding of the orange spectra in the present conditions (particularly, for a 5 mm distance between source and detector). It was found that the whole orange spectra are mainly determined by the peel's spectrum, whose absorption component, in turn, is well approximated by the spectrum of water. It is important to stress that our results are valid only for 5 mm distance between source and detector fibers. Hence, the acquisition of spectra with larger distances should be considered as future work. Moreover, the understanding of the differences between the experimental spectra and the best fit could be related to the composition of the peel, namely carbohydrates.

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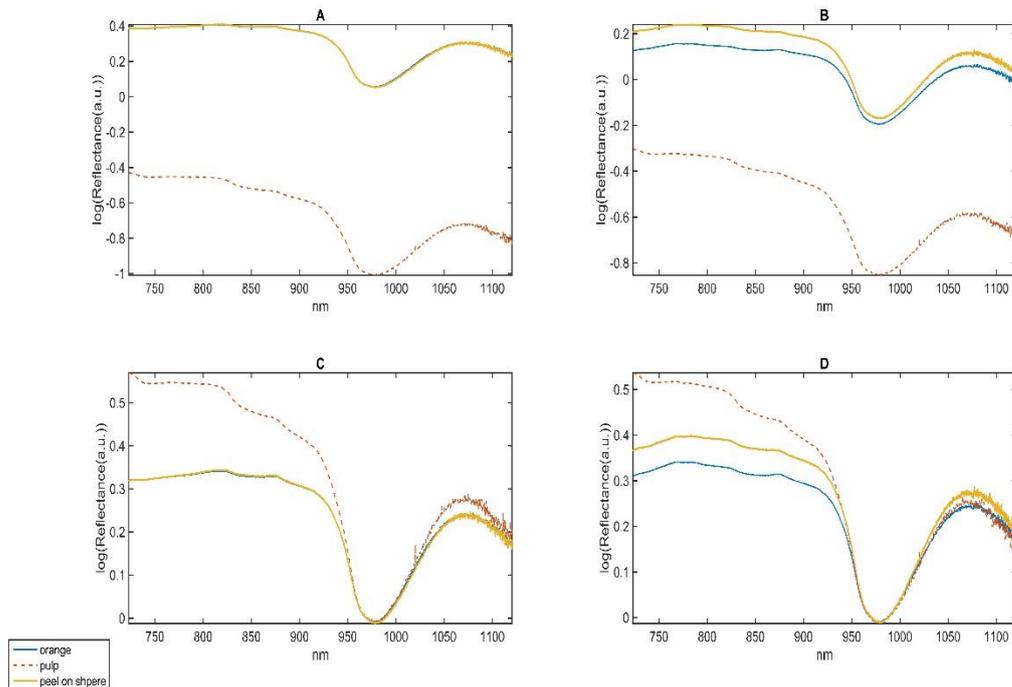
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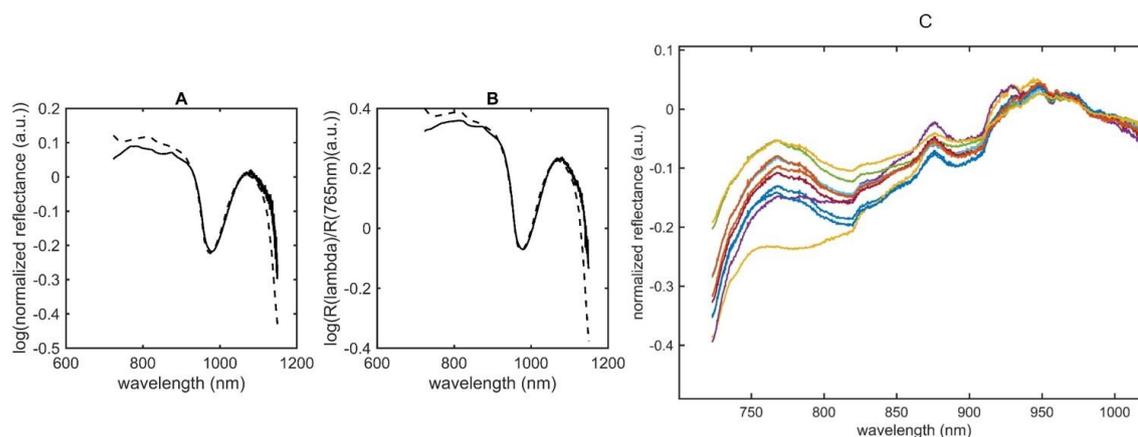
### Tables and Figures

**Table 1.** Water content and relative turgidity.

Orange	units	1	2	3	4	5	6	7	8	9	10
<b>Water content</b>	%	68.5	63.2	74.9	61.1	71.7	67.9	67.2	73.2	67.0	62.4
<b>Relative turgidity</b>	%	57	57	60	59	57	62	57	63	52	51



**Figure 1.** Representation of the normalized reflectance spectra of whole orange (yellow), pulp (dashed red and peel (blue) of two different oranges (A and B). Water content of these oranges is respectively: 71 and 75 %. Relative turgidity is respectively: 60 and 57%.



**Figure 2.** A and B: Water best fit spectrum to the experimental spectrum obtained for two oranges. The water content is 62 and 61 % respectively. The obtained values of  $\mu_a$ ,  $\mu'_s$  and  $k$  for both cases are respectively:  $0.56 \cdot \mu_w \text{ mm}^{-1}$ ,  $1.3 \text{ mm}^{-1}$  and  $-0.45$ ; and  $0.67 \cdot \mu_w \text{ mm}^{-1}$ ,  $1.7 \text{ mm}^{-1}$  and  $0$ . C- Difference between the experimental spectra and the obtained through the water best fit for ten oranges.