

Abstract

Identification of water matrix coefficients in mushrooms (*Agaricus bisporus*) using robust ensemble of Monte Carlo uninformative variable elimination

C. Esquerre,^{a,b,*} A.A. Gowen,^b R. Tsenkova,^c C.P. O'Donnell^b and G. Downey^a

^aAshtown Food Research Centre, Teagasc, Dublin 15 Ireland

^bUniversity College Dublin, Dublin 4 Ireland. E-mail: Carlos.Esquerre@teagasc.ie

^cBiomeasurement Technology Laboratory, Faculty of Agriculture, Kobe University, Kobe, Japan

Introduction

The high moisture content of mushrooms makes them potentially interesting to study from an Aquaphotomics perspective. The aim of this work was to investigate the spectral behaviour of mushrooms under physical perturbation (different levels of mechanical vibration), to identify water bands which relate to perturbations (water matrix coordinates, WAMACS) and to study the changes in absorbance at these wavelengths under perturbation. The objective of this work was to use single point and imaging spectroscopy to identify WAMACS in mushrooms.

Materials and methods

For the point spectroscopy study, spectra were collected in reflectance mode using an NIRSystems 6500 instrument over the wavelength range 400–2498 nm at 2 nm intervals. Mushrooms were subjected to physical damage by controlled vibration (400 rpm) in a plastic box for 10 minutes. These mushrooms were labelled “damaged” and untreated mushrooms labelled “undamaged”. After spectra were taken at time 0 h mushrooms were left at room temperature conditions ($20 \pm 2^\circ\text{C}$), and sequentially analysed at times 1 h, 2 h, 3 h and 4 h (“storage” perturbation). For the chemical imaging experiments, spectra were obtained using a pushbroom line-scanning instrument, operating in the NIR (950–1700 nm) wavelength range. The perturbation examined in this

study was vibration of mushrooms at a vibration speed of 400 rpm using a reciprocating vibration table for five different time periods: 0 s, 60 s, 120 s, 300 s and 600 s (“damage time” perturbation). Objective identification of water matrix coefficients can be regarded as one of the most challenging tasks in Aquaphotomics. In this work, two methods were applied and compared: (i) Selection based on PLS regression vectors (turning or inflection point); (ii) variable selection using robust ensemble of Monte Carlo uninformative variable elimination. Variable importance in projection (VIP) and second derivative spectra were also considered.

Results and discussion

Candidate water matrix coordinates were selected using methods I and II and tentative assignments were made. For point spectroscopy experiments, the data were pre-treated by SNV over the second derivative to control the change in the baseline and the scatter effect. The total water content over time decreased. This was reflected in decreasing free water (1396–1398 nm and 1406 nm) bands. For undamaged mushrooms the signal decreased for the first two bands and increased for the third; for damaged mushrooms the first band (1412 nm) was not relevant and the second and third bands (1460 and 1510) increased. The trend (increase) in damaged mushrooms at the 1460 nm band was weaker than at other bands. This may have been due to a cross effect between formation of melanin compounds (N-H bond) and reduction of water molecules with one hydrogen bond for the damaged mushrooms. For the chemical imaging experiments, EMSC was applied to absorption spectra to decrease scattering effects and PLSR models were built to predict damage time. The largest regression coefficient occurred at 1398 nm, which may be related to the presence of “free” or “weakly bound” water on the mushroom surface after vibration. The “free” water increased with damage intensity due to the release of cellular water content following the disruption of cellular walls after vibration damage; correspondingly, the absorption at the band at 1454 (more “bound” water) decreased with damage intensity. Another large regression coefficient occurred at 1433 nm. This may have been due to the 1st overtone donor-donor-acceptor (DDA) asymmetric stretch (OH–H₂O). The opposing trends in absorption observed in the point and imaging spectroscopy studies can be explained as follows: the “damage time” perturbation (imaging spectroscopy) results in water release, the greater amount of water leading to less strongly bound water, and the “storage” perturbation point spectroscopy) results in water loss leading to an increase in the bond strength. The Monte Carlo re-sampling strategy can be employed as a useful aid in Aquaphotomics, enabling identification of the most stable and relevant regression coefficients.