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A non-destructive determination of peroxide values, total nitrogen and mineral nutrients in an edible tree nut using hyperspectral imaging

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ABSTRACT

Nuts are nutritionally valuable for a healthy diet but can be prone to rancidity due to their high unsaturated fat content. Nutrient content of nuts is an important component of their health benefits but measuring both rancidity and nutrient content of nuts is laborious, tedious and expensive. Hyperspectral imaging has been used to predict chemical composition of plant parts. This technique has the potential to rapidly predict chemical composition of nuts, including rancidity. Hence, this study explored to what extent hyperspectral imaging (400–1000 nm) could predict chemical components of *Canarium indicum* nuts. Partial least squares regression (PLSR) models were developed to predict kernel rancidity using peroxide value (PV) for two different batches of kernels, and macro- and micronutrients of kernels using the spectra of the samples obtained from hyperspectral images. The models provided acceptable prediction abilities with strong coefficients of determination (R^2) and ratios of prediction to deviation (RPD) of the test set for PV, first batch ($R^2 = 0.72$; RPD = 1.66), PV, second batch ($R^2 = 0.81$; RPD = 2.30), total nitrogen ($R^2 = 0.80$; RPD = 1.58), iron ($R^2 = 0.75$; RPD = 1.46), potassium ($R^2 = 0.51$; RPD = 0.94), magnesium ($R^2 = 0.81$; RPD = 2.04), manganese ($R^2 = 0.71$; RPD = 1.84), sulphur ($R^2 = 0.76$; RPD = 1.84) and zinc ($R^2 = 0.62$; RPD = 1.37) using selected wavelengths. This study indicated that visible-near infrared (VNIR) hyperspectral imaging has the potential to be used for prediction of chemical components of *C. indicum* nuts without the need for destructive analysis. This technique has potential to be used to predict chemical components in other nuts.

1. Introduction

Nuts are a nutritious food and contribute greatly to human health by reducing cardiovascular disease (Ros, 2009). Nuts are generally high in protein and rich in essential macro- and micro-nutrients, and are recommended as part of a balanced diet (Ros, 2009). Nut macro- and micro-nutrients are usually influenced by both plant variety and origin of the nut (Anderson and Smith, 2005). Nutrient content of different nut species also varies significantly (Ros, 2010). For example, whilst almond is rich in calcium (250 mg/100 nut), pistachio is rich in potassium (1030 mg/100 nut) (Ros, 2010). It is important for consumers to calculate their daily nutrient intake if they are seeking to compensate their daily nutrient intake naturally rather than using supplements. The current chemical analyses of the nuts require nuts to be destroyed to create homogenised samples and are both expensive and time-consuming.

Unsaturated fats and oils in nuts are prone to rancidity throughout storage and/or post-harvest handling and processing (Alasalvar et al., 2010; Bai et al., 2017). Rancid nuts develop off-flavours and are considered a major issue in nut industries (Alasalvar et al., 2010). Food rancidity is also associated with food-borne disease and rapid food assessments are sought to address this issue. Rancidity occurs through various mechanisms, one of which is autoxidation which generates hydro-peroxides (Özdemir et al., 2001; Walton et al., 2017). Hydroperoxides can react with other nut components and/or decompose leading to unwanted substances including alcohols (Özdemir et al., 2001). Peroxide value (PV) assessment is a simple titration method used worldwide (AOAC, 2000). However, assessing PV of the nuts requires oil extraction which is destructive and time-consuming.

New non-destructive technologies to assess food quality, including the use of hyperspectral imaging, are rapidly developing (Ariana et al., 2006; ElMasry et al., 2007; Kamruzzaman et al., 2012).

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Hyperspectral cameras capture a set of images within narrow bands from an object simultaneously or sequentially within a specified range of the light spectrum, providing both spectral and spatial information of an object (Manley, 2014). The spectral and spatial information collected from an object allows the identification of both location and chemical compounds in an object without a need to have homogenised the object (Manley, 2014). Although various wavelengths, between 350 nm and 1700 nm, have been examined in different studies to predict food and crop quality, the most used wavelengths are between 400 nm and 1000 nm (Ariana et al., 2006; Gama et al., 2018a; Mahesh et al., 2015).

Whilst hyperspectral imaging has been used to assess fruit and vegetable qualities, edible nut kernels have been less studied (Mahesh et al., 2015; Gama et al., 2018a). For example, hyperspectral imaging has been used to predict crude protein (calculated as nitrogen concentration × 6.25) (Bai et al., 2017; Chew et al., 2011) or to predict macronutrients including N, P and K in different plant tissues and soil samples (Gama et al., 2018a; Tahmabian et al., 2018a,b; Zhang et al., 2015, 2013). Multispectral imaging has been used to predict PV of butter cookies (Xia et al., 2015). The PV of macadamia nuts has been predicted using NIR spectroscopy (Canneddu et al., 2016), whilst nitrogen concentration of almonds has been predicted using hyperspectral imaging (Gama et al., 2018a) but, to the best knowledge of the authors, there is no study available to predict PV of nuts using hyperspectral imaging. The selected important wavelengths can be further used to develop multispectral imaging cameras (Kamruzzaman et al., 2016). The multispectral cameras can be then used in the nut industry. The main objective of this study was to explore to what extent hyperspectral imaging can be used to assess kernel PV, nitrogen and nutrient concentration of nuts. In this study, *Canarium indicum* (Burseraceae) (Fig. 1a) kernels were used that were rich in protein and micro-nutrients but were also prone to rancidity due to high oil content (Walton et al., 2016a,b; Walton et al., 2017).

2. Methods and materials

2.1. Sample preparation

Ripe *C. indicum* fruits were sourced from Kerevat, East New Britain, Papua New Guinea (PNG) in 2015 and 2016. The fruits were de-pulped by soaking in warm water for 5 min. The nuts were dried in a laboratory fan-forced oven and manually cracked. The testa of the kernels was removed by blanching in hot water at 100 °C for 90 s and squeezing manually (Walton et al., 2016a). Two batches of kernels, with different thermal treatments, were used to predict PV in this study to obtain a continuous range of PV. In the first batch, 246 kernels were divided into three thermal groups and each group was heated in an oven at 110 °C, 120 °C or 150 °C for 10 min. The kernels were then divided into the groups of 3 kernels (from the same thermal group) for capturing hyperspectral images (82 images).

The second batch of kernels, 642 kernels, was divided into four thermal groups. The thermal groups received different heat treatments including (a) fresh with no heat treatment (150 kernels); (b) accelerated ageing in the oven at 45 °C for 24 days in dark (168 kernels), (c) stored at 24 °C for 12 months and subsamples were collected every four months (162 kernels); and (d) stored at 4 °C for 12 months and subsamples were processed every four months (162 kernels). The kernels were divided into groups of six kernels prior to the thermal treatments. in total, 107 hyperspectral images were captured. The kernels used at each image were bulked to constitute a sample for chemical analyses (Figs. 1 and 2).

2.2. Kernel chemical analysis

The peroxide value (PV) of the kernels in both batches were determined using the titration method provided in AOAC Official Method 965.33 (AOAC, 2000) with a slight modification to be used for micro-titration. In brief, 5 ml $CH_3COOH/CHCl_3$ was added to 1 g of oil and gently agitated until it dissolved and then 0.1 ml of saturated KI solution was added. The mixture was shaken for 1 min before adding 6 ml deionised water. The mixture was then titrated using 0.01 M $Na_2S_20_3$. The PV has been expressed as milliequivalents of O_2 kg^{-1} oil in this study.

Kernel total nitrogen (TN) concentration of the first batch of kernels was determined using a combustion method (Chew et al., 2011). The kernel iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sulphur (S) and zinc (Zn) concentrations of the first batch of kernels were determined using digestion in an open-vessel with a 5:1 mixture of nitric and perchloric acids. Afterwards, the nutrients were determined using ICPOES (Bai et al., 2015).

2.3. Hyperspectral imaging system

Two visible near-infrared (VNIR) hyperspectral imaging systems operated in the spectral region of 400–1000 nm were employed to capture images of the kernels in the reflectance mode. The first hyperspectral imaging system, located at Spectral Imaging Laboratory at Griffith University, consisted of a hyperspectral filter, VA210-.40-1.0-L AOTF hyperspectral video adapter, a VFI-142.5-155-SPF-B2-C2/ext-X-Y-Z 2-Channel SPF AO Controller Unit manufactured by Brimrose Corporation of America, and a BM-141GE camera from JAI. Four 650 W halogen lights in a square configuration in the horizontal plane at a

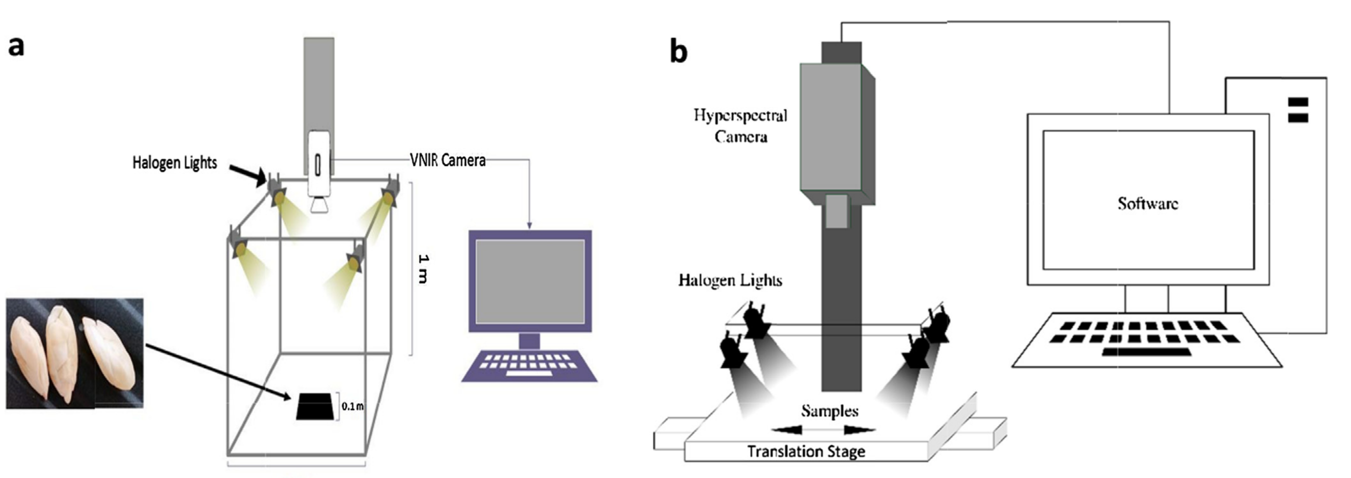

Fig. 1. A schematic graph of the image acquisition used (a) in the first batch and (b) the second batch of samples.