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Assessment of physico-chemical traits related to eating quality of young dairy bull beef at different ageing times using Raman spectroscopy and chemometrics

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ABSTRACT

Raman spectroscopy and chemometrics were investigated for the prediction of eating quality related physico-chemical traits of Holstein-Friesian bull beef. Raman spectra were collected on the 3rd, 7th and 14th days post-mortem. A frequency range of 1300–2800 cm^{-1} was used for partial least squares (PLS) modelling. PLS regression (PLSR) models for the prediction of WBSF and cook loss achieved an R^2CV of 0.75 with RMSECV of 6.82 N and an R^2CV of 0.77 with RMSECV of 0.97%w/w respectively. For the prediction of intramuscular fat, moisture and crude protein content, R^2CV values were 0.85, 0.91 and 0.70 with RMSECV of 0.52%w/w, 0.39% w/w and 0.38%w/w respectively. An R^2CV of 0.79 was achieved for the prediction of both total collagen and hydroxyproline content, while for collagen solubility the R^2CV was 0.88. All samples (100%) from 15- and 19-month old bulls were correctly classified using PLS discriminant analysis (PLS-DA), while 86.7% of samples from different muscles (*longissimus thoracis*, *semitendinosus* and *gluteus medius*) were correctly classified. In general, PLSR models using Raman spectra on the 3rd day post-mortem had better prediction performance than those on the 7th and 14th days. Raman spectroscopy and chemometrics have potential to assess several beef physical and chemical quality traits.

1. Introduction

Meat quality is a complex concept that involves intrinsic cues (i.e. safety, shelf-life, nutritional value, eating quality) and extrinsic cues (i.e. brand, quality label, origin, convenience of the product). Of these, eating quality is a critical parameter to determine consumer preferences, including sensory quality (i.e. tenderness, juiciness and flavour) and physico-chemical traits: technological quality (i.e. Warner-Bratzler shear force (WBSF) and cook loss; compositional quality (i.e. intramuscular fat (IMF), collagen and moisture content) (Prieto et al., 2009; Troy & Kerry, 2010).

The amount and solubility of intramuscular connective tissue (IMCT) and post-mortem proteolysis of myofibrillar proteins influence beef tenderness predominately. Collagen, as a major component of IMCT, is believed to contribute to the "background" toughness of beef after prolonged ageing. It has been generally accepted that higher levels of total collagen and particularly lower collagen solubility are associated with reduced beef tenderness (Jeremiah et al., 2003a). IMF produces marbling effects in beef, which is positively linked to beef tenderness, juiciness and flavour (Scollan et al., 2006). A higher level of moisture in beef can lead to higher cook loss and lower tenderness (Chambaz et al., 2003). An increased cook loss has a negative effect on beef tenderness (Silva et al., 1999).

Ageing is the most influential primary processing factor involving complex changes in muscle metabolism in the post slaughter period. Post-mortem proteolysis is a pronounced action during ageing, which greatly contributes to meat tenderization (Muchenje et al., 2009). Moreover, water mobility and biomechanical changes of IMCT in meat during ageing are also associated with changes in quality parameters, including juiciness and tenderness (Pearce et al., 2011; Nishimura, 2015).

Previous studies have demonstrated the potential of Raman spectroscopy (RS) combined with chemometric approaches to measure WBSF and cook loss of aged meat. A regression coefficient determination of cross validation (R^2CV) of 0.75 for the prediction of shear force (SF) in roasted beef silversides was reported by Beattie et al. (2004)

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while R^2CVs of 0.33–0.79 were obtained for the prediction of intact fresh bovine *gluteus medius* (GM) muscles SF at the 14th day post-mortem using a portable Raman system (Bauer et al., 2016). R^2CVs of 0.79–0.86 for SF and 0.79–0.83 for cook loss were obtained for intact frozen/thawed sheep meat after ageing for 5 days using a prototype handheld Raman system (Schmidt et al., 2013). In contrast, a very low R^2CV of 0.06 was obtained using a handheld Raman device for SF prediction on intact fresh lamb muscle at the 1st day post-mortem by Fowler et al. (2014). However, none of these studies have reported on homogenized meat samples, and previous studies only focused on one type of muscle and one specific ageing time; the prediction ability for different muscle types and different ageing times has not been investigated to date.

A rapid and applicable method for compositional quality assessment would be highly appreciated by the meat industry. Near infrared spectroscopy (NIRS) has been employed to predict chemical composition of beef with R^2CVs of 0.16–0.82 for predictions of crude protein (Alomar et al., 2003; Ripoll et al., 2008), R^2CVs of 0.76–0.99 for IMF (Rødbotten et al., 2000; De Marchi et al., 2007), R^2CVs of 0.09–0.91 for moisture (Cozzolino et al., 2002; De Marchi et al., 2007) and R^2CVs of 0.18–0.44 were reported for collagen prediction (Alomar et al., 2003; De Marchi et al., 2007). Hyperspectral imaging has been reported to be effective for the prediction of hydroxyproline content in chicken meat (R^2CV - 0.87) (Xiong et al., 2015). Compared with NIRS, RS has been claimed to provide more detailed information on chemical structures and physical forms for the identification of substances by their characteristic spectral patterns – 'fingerprinting' and for quantitative detection of the amount of a substance in a sample (Smith & Dent, 2005). However, recent studies using RS on lamb were unable to predict collagen and for IMF obtained an R^2CV of 0.02 (Fowler et al., 2015). The authors of this study are not aware of any previous research investigating the use of RS to determine chemical composition of beef particularly for collagen characteristics. Moreover, the previous studies were mainly focused on sole physical or chemical trait of meat, while the prediction performance of RS on a wide range of beef physical and chemical traits has not been explored.

Beef quality can also be largely affected by on-farm production factors, such as animal breed, slaughter age, sex, feeding regime, muscle location etc. (Frylinck et al., 2013). The clear discrimination of beef according to production factors could not just solely be used to identify meat origin, but also as a marker to select meat cuts based on expected quality properties. In addition to the conventional analytical methods for muscle identification such as DNA, immunological and chromatographic techniques, RS has been shown to be a potential tool for rapid assessment of food adulteration and discrimination between species and muscle groups within species (Herrero, 2008; Damez & Clerjon, 2008).

The objectives of this study are to use RS and chemometrics to (1) develop models for the prediction of key physico-chemical traits of young bull beef; (2) select the most representative wavelengths for these predictions; (3) compare prediction performance during beef ageing; (4) discriminate beef samples from three muscle types or from two slaughter ages.

2. Materials and methods

2.1. Source of materials

For the prediction models, Holstein-Friesian (HF) bulls (n = 49) were slaughtered in a commercial abattoir. The *longissimus thoracis* (LT) muscle samples were removed from the carcasses of 35 bulls at 48 h post-mortem at 4 °C. LT and *semitendinosus* (ST) muscles were removed from the carcasses of the remaining 14 bulls. At 72 h post-mortem, muscle samples (n = 63) were cut into individual slices (~25 mm thick) and vacuum-packed using five-layer (PA/tie/PE/tie/PE) coextruded nanocomposite films (Versatile Packaging Ltd., Ireland) and a VG 400 ILPRA sealing machine (Vigevano, Italy). Samples for chemical analysis and Raman spectra measurement on the 3rd day post-mortem were immediately stored at − 20 °C; while samples for Raman spectra measurements at the 7th and 14th days post-mortem were aged for 7 and 14 days at 4 °C respectively and then stored at − 20 °C.

For the discrimination models, 30 bulls were slaughtered at 15-months (n = 15) and 19-months (n = 15) of age respectively. LT, ST and GM muscles were collected from 10 bulls (15-months of age), and were used for muscle type discrimination. For age discrimination, 26 muscles (LT & ST) were collected from 15-month old bulls, and 29 muscles (LT & ST) were collected from 19-month old bulls. Two individual slices were cut from each muscle and vacuum-packed after ageing for 7 and 14 days at 4 °C respectively, and then frozen at − 20 °C prior to Raman spectra measurements.

2.2. Warner-Bratzler shear force and cook loss

Trimmed beef steaks which had been aged for 3 days (150–180 g) were thawed in constantly circulating water at 10 to 15 °C. The steaks were then cooked in open bags suspended in a water bath (TC120, Grant Instruments Ltd., England) at 72 °C until the temperature in the centre of the steak reached 70 °C. Cook loss was determined as:

$$((raw\ weight - cooked\ weight)/raw\ weight) \times 100\%.$$

Steaks were immediately cooled and held overnight at 4 °C. Seven meat cores (12.5 mm diameter) were cut parallel to the longitudinal orientation of the muscle fibres for each sample. When the cores reached room temperature, they were sheared using the Warner-Bratzler (WB) shear blade attached to an Instron Universal Testing Machine (Models 5543, Instron (UK) Ltd., High Wycombe, UK). A 500 N load cell was used with a crosshead speed 50 mm/min. The average maximum shear force was calculated by excluding the two extreme values from seven acquisitions.

2.3. IMF, moisture and protein

Frozen samples which had been aged for 3 days were thawed at 4 °C for ~16 h. After all external fat was trimmed the lean beef and exudate were homogenized together using a blender (R301 Ultra, Robot Coupe SA, France). Moisture and IMF concentrations were measured using a smart microwave moisture drying oven and an NMR Smart Trac rapid Fat Analyser (CEM Corporation, USA) using AOAC official method 985.14 (AOAC, 1991). Protein concentration was determined using a LECO FP328 (LECO Corp., MI, USA) protein analyser based on the Dumas method according to AOAC method 992.15 (AOAC, 1992). All composition tests were carried out as two determinations per sample with a standard deviation between replicates below 1.00%.

2.4. Collagen content and solubility

Samples which had been aged for 3 days were freeze dried and then milled to a fine homogenate. Approximately 4 g of muscle homogenate was defatted using 20 mL of diethyl ether overnight and re-dried. The heat-soluble collagen was extracted as described by Hill (1966) with slight modifications. Briefly, 2.5 g of fat-free dry (FFD) muscle hydrolysate was heated in water bath for 2 h at 90 °C with 15 mL of Ringer's solution. Sample solution was centrifuged (LYNX 6000, Thermo Scientific) twice at 3990*g* for 10 min at room temperature. The supernatants from the two centrifugations were combined. Then 100 μL of final supernatant and 3 mg of FFD (total collagen) of each muscle (in triplicate) were hydrolysed using 2 mL of 6 M HCl under nitrogen in sealed vials at 110 °C overnight. Following hydrolysis, the vials were cooled and centrifuged (5174C/R, Eppendorf, UK) at 18,187*g* for 1 min at room temperature to remove particulate matter.

Quantitative analysis of hydroxyproline in FFD muscle hydrolysates was carried out using LC-MS/MS with slight modifications of the method reported by Colgrave et al. (2008). Briefly, 100 μL aliquots of