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The potential of laser-induced breakdown spectroscopy for industrial at-line monitoring of calcium content in comminuted poultry meat

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ABSTRACT

The presence of bone particles, and hence the calcium content, is a key quality parameter for mechanically separated poultry meat (MSM). A method for fast at-line monitoring of the calcium content in MSM during production is therefore requested by the industry. Laser-induced breakdown spectroscopy (LIBS) is an interesting technique in this regard because it is fast and potentially enables direct detection of minerals in a sample with minimal sample preparation. Nine commercial MSM samples, representing the common range of calcium contents in MSM, a hand-deboned sample and minced poultry meat were measured by LIBS using sample preparation suitable for an industrial at-line monitoring setting. In the spectra obtained, emission lines from sodium, potassium and calcium were identified. Using inductively coupled plasma optical emission spectrometry (ICP-OES) as the reference method, and partial least squares regression (PLS) as calibration model, including three calcium lines adjusted by potassium, it was possible to separate samples according to three calcium levels with LIBS. Very low (<20 mg/100 g Ca), intermediate (20–90 mg/100 g Ca), and high (>90 mg/100 g Ca).

1. Introduction

An increased demand for white meat and the possibility to increase the value of secondary products have driven the poultry meat industry towards increased production of mechanically separated poultry meat (MSM) (Viuda-Martos, Fernández-López, & Pérez-Álvarez, 2012). MSM is a product obtained by applying mechanical forces to separate meat residues from the various carcass parts that remain after removing the primal meat cuts from a chicken. Depending on the carcass part and the type of deboning equipment used, a large range of comminuted products can be obtained, which differ in chemical composition as well as textual characteristics (Barbut, 2002). A key parameter to distinguish the different MSM qualities is calcium as this is a marker of bone residues present in the final product. According to EU Regulation ((EC) No 2074/2005) calcium content of MSM must not exceed 1000 ppm of fresh product, measured by a standardized international method. The calcium content depends highly on the force applied during processing as well as the type of processing equipment and raw materials used, which again affects the yield and MSM quality (Branscheid & Judas, 2011; EFSA Panel on Biological Hazards, 2013).

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique in which a small amount of material, typically a few μg, is ablated by a laser pulse. The formed plasma contains a mixture of exited neutral and charged atomic and molecular species and it is the light emissions from these that are measured as they return to their ground state (Fortes, Moros, Lucena, Cabalín, & Laserna, 2012). The method can be used for rapid measurement of the mineral composition in a sample and is well suited for production monitoring. Little to no sample preparation is required, it is minimally destructive and enables direct measurement from a distance (Noll et al., 2014). However, there are also several challenges associated with this method for quantitation. The signal intensities in LIBS depend heavily on the physical and chemical properties of the sample, of which the chemical composition as well as the homogeneity/particle size of the sample surface are particularly important. These conditions determine how the laser interacts with the sample and thereby the plasma temperature, which together with the amount of ablated material largely affects the relative intensities of emission lines (Fortes et al., 2012; Lei et al., 2011). The

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term sample matrix is used in this paper for the variations in the LIBS signal not caused by variations in elemental composition, but by the chemical and physical properties of a sample.

Within food research, LIBS is still in its infancy. The method has been applied for quantitative or qualitative exploration of the mineral composition in milk powder (Lei et al., 2011), breakfast cereals (Ferreira et al., 2010), wheat grains (Martelli, Brygo, Sadoudi, Delaporte, & Barron, 2010), bakery products (Bilge, Boyacı, Eseller, Tamer, & Çakır, 2015; Ferreira et al., 2010; Kim, Kwak, Choi, & Park, 2012) and a few fresh fruits and vegetables (Beldjilali et al., 2010; Juvé, Portelli, Boueri, Baudelet, & Yu, 2008; Kim et al., 2012). No prior studies on fresh food of animal origin have been reported, most likely due to the low signal-to-noise (S/N) spectra obtained from LIBS on this type of samples. One study has been conducted on powdered reference material, mainly liver samples, pressed into pellets (Santos Jr et al., 2012) and on freeze-dried oyster samples (Akpovo et al., 2013). Several of the food studies have demonstrated that Ca I and II emission lines of various wavelengths can be used alone or in combination with other spectral features to quantify the calcium content (Beldjilali et al., 2010; Ferreira et al., 2010; Kim et al., 2012; Santos Jr et al., 2012). However, the sample preparation performed in the majority of these studies, which typically included drying and pressing into pellets, precludes them for at-line use in a production setting.

In the present study, we report on the potential of LIBS for quality control of fresh MSM poultry meat. Contrary to previous studies, it is investigated if it is possible to deduce information despite poorer S/N spectra by means of data pre-processing. To approximate an industrial application, fresh commercial samples that represent the typical range of calcium levels in MSM are measured. The performance of LIBS for measuring the calcium content as well as the ability to distinguish between different types of MSM are explored using inductively coupled plasma optical emission spectrometry (ICP-OES) as the reference method.

2. Materials and methods

2.1. Analyzed samples

In the selection of samples, priority was given to cover the main sources of variation that influence the calcium content of MSM in a production setting. Therefore, a range of commercial samples representing different types of deboning equipment, carcass parts and pressures applied during processing were selected as outlined in Table 1.

For comparison of calcium content between MSM and non-MSM meat, regular breast meat and hand deboned breast carcass meat were also measured (Table 2). The effect of the particle size of minced meat on the LIBS measurement was investigated by measuring emulsified and minced breast meat as well as a mixture of the two. Finally, the ability of LIBS to discriminate different calcium levels within the same sample was investigated by an enrichment experiment in which two production samples (BH and D) were enriched with 50 mg/100 g and 100 mg/100 g calcium by adding 0.75 and 1.50 g/100 g milled dried poultry bone meal (Farmfood BHJ, Gråsten, Denmark), respectively, to the samples (sample IDs BH-50, BH-100, D-50 and D-100).

All production samples were provided by the two abattoirs Danpo (Aars, Denmark) and HKScan Denmark A/S (Vinderup, Denmark). Samples were collected during April–July 2014. On the day of sample collection, samples were frozen and they were stored at −20° until the day of analysis.

Table 1
List of analyzed MSM meat samples.

Carcass part	Pressure	Sample ID
Breast	Low	AL
	Medium	AM
Breast, upper backs and necks without skin	High	AH
Upper backs and necks	Medium	BM
Upper backs and necks without skin	High	BH[a]
Backs	High	F
Drumstick (bone removed)	Low	D[a]
Necks without skin	Low	N
Caps without skin	Low	C

[a] Samples were also analyzed as enriched samples with 50 or 100 mg added calcium per 100 g sample. Enriched samples are designated D-50/BH-50 and D-100/BH-100, respectively, for the two levels of enrichment.

2.2. LIBS analysis

The LIBS setup consisted of a CFR400 frequency doubled Nd:YAG laser (Quantel, Bozeman, Montana) and an echelle-type Aryelle 200 spectrometer (Lasertechnik Berlin, Berlin, Germany) equipped with a 1024 × 1024 pixels CCD detector (Andor, Belfast, United Kingdom) that was cooled to −67 °C during measurements. The laser had a pulse energy of 230 mJ and a duration of 9 ns at 532 nm and was focused on the sample using a 15 cm focal length lens, giving an estimated spot diameter of ≈0.7 mm at optimal focus. Due to the uneven surface and variation in sample composition, the actual spot size, and hence laser irradiance, fluctuated. The light emitted from the plasma was collected using a 4 cm focal length lens located about 5 cm from the target at an angle of 31° from the laser axis. The spectrum was recorded in the range between 200 and 800 nm. The delay time between the laser pulse and the light collection was 3 μs.

Before the LIBS measurements, samples were thawed at 5 °C, stirred to mix the meat juice back into the sample and put into quadratic weighing dishes. As the objective was to investigate the feasibility of a potential industrial application, the only preparation of the samples consisted in covering these with plastic wrap and pressing them flat upside down on a table to make the surface as even as possible. A similar preparation could easily be applied automatically in an actual industrial application. Samples were stored on ice until the time of measurement. Each sample was measured at 25 points on the surface in a 5 × 5 grid pattern of approximately 9 cm^2. The spectrum recorded for each point measurement was the sum of 15 successive shots. Between each shot, the sample was moved by an automated XY stage to expose a fresh surface for the following laser pulse. Two examples of sample surfaces after measurement are shown in Fig. 1. The collecting and focusing lenses were cleaned from meat juice using de-ionized water and a cleansing agent between each sample. For each seven to eight samples an automated wavelength calibration was performed using a mercury lamp (Lasertechnik Berlin, Berlin, Germany).

All MSM and non-MSM samples were measured on one day, while the enrichment experiment was conducted on a separate day. For both days, samples were measured in randomized order within each of five repetitions so that all sample types were measured before measuring the second replicate of each sample, etc. The instrument was disassembled to clean it thoroughly between the first and the second day of measurements. As LIBS measurements are generally very sensitive to even the minor changes in the positioning of the lenses that could not be eliminated in the LIBS setup between day one and day two, the results from the two measurement days were not directly comparable. Results from day one and day two will therefore only be considered separately. In a designated industrial setup, this effect can conceivably be minimized.