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1 **Quantification of rubidium as a trace element in beef using laser induced breakdown spectroscopy**

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18 **Keywords:** LIBS, minced beef, rubidium, PLSR, chemometrics.

19

20 **Abstract.**

21

22 This study evaluates the potential of laser induced breakdown spectroscopy (LIBS) coupled with
23 chemometrics to develop a quantification model for rubidium (Rb) in minced beef. A LIBSCAN 150
24 system was used to collect LIBS spectra of minced beef samples. Beef liver was used to spike the Rb
25 levels in minced beef. All samples were dried, powdered and pelleted using a hydraulic press.
26 Measurements were conducted by scanning 100 different locations with an automated XYZ sample
27 chamber. Partial least squares regression (PLSR) was used to develop the calibration model, yielding a
28 calibration coefficient of determination (R_c^2) of 0.99 and a root mean square error of calibration (RMSEC)
29 of 0.05 ppm. The model also showed good results with leave-one-out cross validation, yielding a cross-
30 validation coefficient of determination (R_{cv}^2) of 0.90 and a root mean square error of cross-validation
31 (RMSECV) of 0.22 ppm. The current study shows the potential of LIBS as a rapid analysis tool for the
32 meat processing industry.

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36 **1. Introduction**

37 Rubidium (Rb) is a quasi-essential element for living organisms. The human body treats Rb ions similar
38 to potassium ions, concentrating Rb in the body's intracellular fluid (Kékedy-Nagy et al., 2000). A study
39 in 2008 showed that rubidium exhibits anti-depressant properties (Canavese et al., 2008). The daily human
40 intake of Rb is ~3 mg, by foods such as beef, soybeans etc. and drinking water. Beef is a rich source of
41 **important trace elements such as iron, copper, zinc as well as rubidium. Beef** contains **around 27.2 % dry**
42 **matter out of which 6.84 ppm is rubidium** (Fischer, 1997).

43 Laser induced breakdown spectroscopy (LIBS) is an emerging technique in the field of food
44 analysis. Techniques such as ICP-OES (Inductively coupled plasma – Optical emission spectrometry) and
45 AAS (Atomic absorption spectroscopy) have several limitations such as lengthy sample preparation
46 techniques and the use of hazardous chemicals. LIBS offers various advantages such as minimal sample
47 preparation, chemical free process, rapid detection and portability (Bilge et al., 2016; Kongbonga et al.,
48 2014; Moncayo et al., 2016). Additionally, LIBS also offers the advantage of providing spatial
49 information. Recently, LIBS has been evaluated for mineral quantification in various foods. Singh et al.
50 (2016) used LIBS for quantification of minerals in cucurbit seeds. Andersen et al. (2016) used LIBS to
51 quantify calcium content in comminuted poultry meat for detecting bone particles in mechanically
52 separated meat (MSM). The aim of this study is to evaluate the performance of LIBS coupled with
53 chemometrics to develop a quantification model for rubidium (Rb) in minced beef.

54 **2. Materials and methods**

55 *2.1 Sample Preparation*

56 Fresh **striploin** beef steaks and beef liver weighing approximately **500 g** each were purchased from a local
57 butchers shop in Dublin, Ireland. The lean meat from the beef steaks was diced into small cubes; the liver
58 was also diced. All samples were minced separately using a laboratory meat blender (8011G, Waring
59 Laboratory Science, Stamford CT, USA), which was carefully cleaned using an antibacterial washing
60 liquid and dried before each use. Finally, samples were placed overnight in a hot air drying oven
61 maintained at 105 °C using disposable aluminium dishes.

62 On the next day, dried samples were ground into powder form by using a laboratory meat blender
63 (8011G, Waring Laboratory Science, Stamford CT, USA) followed by sieving using a mechanical sieve
64 (**VS 1000, Retsch (U.K.) Limited, Hope valley, U.K.**) with a 103-mesh screen for 10 minutes at 70 rpm.
65 Beef liver was used to spike the Rb levels in the minced beef. Two independent batches (**15 samples per**
66 **independent batch**) with varying percentages of beef liver mixed with lean beef were prepared. Each
67 sample repeated in triplicates comprised of approximately 400 mg of a powdered mixture of lean beef

68 containing 0%, 10%, 20%, 40% and 100 % of liver (w/w). Samples were then pelleted using a hydraulic
69 press (GS01160, Specac Ltd., Orpington, U.K.) by applying a pressure of 10 tonnes for 3 minutes.

70 2.2 Graphite furnace atomic absorption spectroscopy analysis

71 The rubidium content of lean beef and beef liver were determined using a graphite furnace atomic
72 absorption spectrophotometer (GFAAS) (AA240Z, Agilent Technologies, Santa Clara, USA). Sample
73 preparation was carried out using the standard method of AOAC (FP-3) with slight modifications;
74 approximately 1 g of powdered sample was transferred into crucibles and pre-ashed on a hot plate with
75 the careful addition of small drops of purified nitric acid (CAS 7697-37-2, Sigma Aldrich, Inc., Arklow,
76 Ireland) to aid digestion. Once samples were completely charred, they were transferred to a muffle furnace
77 maintained at 550 °C for 5 hours. Ashes were then dissolved into 50 mL volumetric flasks with 1M
78 purified nitric acid (CAS 7697-37-2, Sigma Aldrich, Inc.). A further dilution was performed in order to
79 maintain the mineral concentrations within the GFAAS optimum measuring range for Rb. For
80 quantification, calibration curves were obtained using standard solutions of rubidium (55727, Sigma
81 Aldrich, Inc., Arklow, Ireland). All samples were measured in triplicate.

82 2.3 LIBS spectra acquisition

83 LIBS spectra were recorded using a LIBSCAN 150 system (Applied Photonics Limited, Skipton North
84 Yorkshire, U.K.) which consists of a Q-switched Nd:YAG laser (ultra, Quantel laser, 601 Haggerty Lane
85 Bozeman, MT, USA), a series of six spectrophotometers covering the wavelength range of 185-904 nm
86 and a LIBSCAN 150 head. The head incorporates a miniature CCD camera and 6 lens holders which
87 collect plasma light of different wavelength regions. The laser used for sample ablation had a pulse energy
88 of 150 mJ and a pulse duration of 5 ns operating at 1064 nm. A repetition rate of 1 Hz was employed
89 along with a 1.27 µs gate delay and 1.1 ms integration time in Q-switched mode. The sample was placed
90 at a LTSD (lens to sample distance) of approximately 80 mm to ensure that the laser was focussed onto
91 the sample. Samples were measured by scanning 100 different locations in a 10 X 10 grid pattern while
92 the sample was moved after each shot with an automated XYZ sample chamber (XYZ-750, Applied
93 Photonics Limited, Skipton North Yorkshire, U.K.) by a step size of 0.70 mm.

94 2.4 Data analysis

95 Data analysis was performed using R (R Core Team, 2014). The “pls” package (Mevik et al., 2013) was
96 used for performing PLSR (partial least square regression).

97 Spectral pre-processing is the most important step before performing chemometric bi-linear
98 modelling such as PLSR in order to remove baseline shifts and non-linearities from the acquired spectra
99 (Rinnan et al., 2009). Pre-processing was performed using standard normal variate (SNV) transformation.

100 Processed data in the wavelength range of 774.527 to 784.824 was selected because the Rb peak exists in
101 this region at 780.010 nm. In order to develop the calibration model, the acquired processed data along
102 with the Rb values obtained were subjected to PLSR. The method of leave-one-out was used for cross
103 validation while developing the calibration models in order to avoid either over- or under-fitting of the
104 models. Goodness of **fit** was evaluated by determining both root mean square error of calibration
105 (RMSEC) and root mean square error in cross validation (RMSECV) which provides information about
106 the deviation of models from their reference values (Cama-Moncunill et al., 2016). The corresponding
107 values of both coefficients of determination in calibration (R_c^2) and in cross validation (R_{cv}^2) were also
108 calculated.

109 **3. Results and Discussion**

110 *3.1.1 Graphite furnace atomic absorption spectroscopy analysis*

111 GFAAS was performed to determine the concentration of rubidium in pure lean beef and pure liver
112 samples. Results of GFAAS analysis are illustrated in Table 1. GFAAS results indicate that Rb content in
113 lean beef is generally lower than in beef liver. The results shown in Table 1 were in good agreement with
114 those reported in the literature (Fischer, 1997).

115 *3.1.2 Spectral analysis*

116 Fig. 1a shows the raw LIBS spectra of powdered lean beef and beef liver. Each spectrum corresponds to
117 an average of 100 spectra collected at different locations of the pellet in order to overcome sample
118 heterogeneity. Emission peak related to rubidium in Fig. 1a have been identified at 780.010 nm with
119 reference to the NIST database (Kramida et al., 2015). Rb exists under group 1 of the periodic table,
120 having a single electron in **its** outer shell and allowing LIBS to easily excite the lone electron and detect
121 the element (Scerri, 2007). It is evident from Fig. 1b that the LIBS spectra clearly differentiates samples
122 based on their Rb contents in both batches, which were in confirmation with the GFAAS results shown
123 in Table 1.

124 *3.1.3 Multivariate data analysis*

125 In the current study, PLSR was performed on pre-processed LIBS data in order to develop a calibration
126 model for Rb. PLSR generates linear prediction models by optimising the covariance between spectral
127 data and the reference values (Rb content). In order to do so, it performs decomposition on both the
128 spectral and reference data simultaneously (Dixit et al., 2016; ElMasry et al., 2013).

129 Best model was identified with four PLS components. The model showed a good fit yielding a R_c^2
130 of 0.99 and R_{cv}^2 of 0.90. Moreover, the RMSEC and RMSECV were low yielding values of 0.05 ppm and

131 0.22 ppm respectively. It could be possible to improve model performance in future studies by **optimising**
132 **factors such as laser pulse energy and LTSD** (Radziemski et al., 2006).

133 **4. Conclusions**

134 The present study shows that LIBS can be successfully used to detect and quantify the trace element Rb
135 in minced beef and beef liver. PLSR was used to model the LIBS spectral data along with reference values
136 obtained for Rb using GFAAS. High values of R_{cv}^2 and low values of the corresponding RMSECV
137 confirmed a good fit for the model. LIBS is an emerging technique in the area of food analysis with
138 potential as an at-line monitoring tool for the meat industry. Results from the current study illustrates high
139 potential for LIBS as a rapid technique to detect and quantify **Rb as well as other important** trace elements
140 such as iron, zinc and copper amongst others in various foods. However, factors related to sample surface
141 such as surface homogeneity, chemical composition and particle size can affect the LIBS spectra. **Effects**
142 **due to non-homogeneous sample surface and chemical composition could be reduced by sufficient**
143 **averaging so that a better representation of the sample could be obtained. Furthermore, variation in particle**
144 **size produces a matrix effect which could be reduced with matrix-matched calibration standards.**

145 In order to make LIBS a suitable technique for routine analysis in a food industry further
146 improvements are required such as an automated focusing system for optimized LTSD and use of
147 detectors optimized for the spectral region of interest. Overall, the study demonstrates potential for LIBS
148 as a rapid analysis tool for the meat processing industry.

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196 7. Figure captions

197 **Fig. 1 LIBS spectra: (a) raw spectra of lean beef and beef liver, (b) SNV transformed spectra: from**
198 **top to bottom - rubidium peak at 780 nm for batches 1 and 2. The arrow (↑) indicates the direction**
199 **of increasing content of rubidium.**

200