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

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Abstract.

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

1. Introduction

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

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

2. Materials and methods

2.1 Sample Preparation

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

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

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

3. Results and Discussion

3.1.1 Graphite furnace atomic absorption spectroscopy analysis

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

3.1.2 Spectral analysis

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

3.1.3 Multivariate data analysis

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

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

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

4. Conclusions

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

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

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6. References

- Andersen, M.-B. S., Frydenvang, J., Henckel, P., & Rinnan, Å. (2016). The potential of laser-induced breakdown spectroscopy for industrial at-line monitoring of calcium content in comminuted poultry meat. *Food Control*, 64, 226-233. doi: 10.1016/j.foodcont.2016.01.001
- Bilge, G., Velioglu, H. M., Sezer, B., Eseller, K. E., & Boyaci, I. H. (2016). Identification of meat species by using laser-induced breakdown spectroscopy. *Meat Science*, 119, 118-122. doi: 10.1016/j.meatsci.2016.04.035

160 Cama-Moncunill, R., Markiewicz-Keszycka, M., Dixit, Y., Cama-Moncunill, X., Casado-Gavaldà, M. P.,
 161 Cullen, P. J., et al. (2016). Multipoint NIR spectroscopy for gross composition analysis of
 162 powdered infant formula under various motion conditions. *Talanta*, 154, 423-430.

163 Canavese, C., Decostanzi, E., Bergamo, D., Sabbioni, E., & Stratta, P. (2008). Rubidium, salami and
 164 depression. You cannot have everything in life. *Blood Purification*, 26(4), 311-314. doi:
 165 10.1159/000129657

166 Dixit, Y., Casado-Gavaldà, M. P., Cama-Moncunill, R., Cama-Moncunill, X., Jacoby, F., Cullen, P. J., et
 167 al. (2016). Multipoint NIR spectrometry and collimated light for predicting the composition of
 168 meat samples with high standoff distances. *Journal of Food Engineering*, 175, 58-64.

169 ElMasry, G., Sun, D.-W., & Allen, P. (2013). Chemical-free assessment and mapping of major
 170 constituents in beef using hyperspectral imaging. *Journal of Food Engineering*, 117(2), 235-246.

171 Fischer, P. W. F. (1997). *Trace Elements in Man and Animals--9: Proceedings of the Ninth International*
 172 *Symposium on Trace Elements on Man and Animals*. Ottawa, Canada: Canadian Science
 173 Publishing, NRC Research Press.

174 Kékedy-Nagy, L., & Cordoş, E. A. (2000). Flame atomic emission determination of rubidium in mineral
 175 and well waters using methane–air flame as excitation source. *Talanta*, 52(4), 645-652.

176 Kongbonga, Y. G. M., Ghalila, H., Onana, M. B., & Lakhdar, Z. B. (2014). Classification of vegetable
 177 oils based on their concentration of saturated fatty acids using laser induced breakdown
 178 spectroscopy (LIBS). *Food Chemistry*, 147, 327-331.

179 Kramida, A., Ralchenko, Y., Reader, J., & Team, N. A. (2015). NIST Atomic Spectra Database (Ver.
 180 5.3), [Online]. Retrieved 2016, October 6 <http://physics.nist.gov/asd>

181 Mevik, B.-H., Wehrens, R., & Liland, K. H. (2013). pls: Partial least squares and principal component
 182 regression. *R package version*, 2.4-3.

183 Moncayo, S., Rosales, J. D., Izquierdo-Hornillos, R., Anzano, J., & Cáceres, J. O. (2016). Classification
 184 of red wine based on its protected designation of origin (PDO) using Laser-induced Breakdown
 185 Spectroscopy (LIBS). *Talanta*, 158, 185-191. doi: 10.1016/j.talanta.2016.05.059

186 R Core Team. (2014). R: A language and environment for statistical computing. R Foundation for
 187 Statistical Computing, Vienna, Austria, 2012: ISBN 3-900051-07-0.

- 188 Radziemski, L. J., & Cremers, D. A. (2006). Handbook of Laser Induced Breakdown Spectroscopy. West
189 Sussex, England: John Wiley & Sons.
- 190 Rinnan, Å., van den Berg, F., & Engelsen, S. B. (2009). Review of the most common pre-processing
191 techniques for near-infrared spectra. *TrAC Trends in Analytical Chemistry*, 28(10), 1201-1222.
- 192 Scerri, E. R. (2007). *The periodic table: its story and its significance*. NY, USA: OUP
- 193 Singh, J., Kumar, R., Awasthi, S., Singh, V., & Rai, A. (2016). Laser Induced breakdown spectroscopy:
194 A rapid tool for the identification and quantification of minerals in cucurbit seeds. *Food*
195 *Chemistry*.

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