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Elemental analysis of fish feed by laser-induced breakdown spectroscopy

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ABSTRACT

In this study, the potential of laser-induced breakdown spectroscopy (LIBS) as an efficient multi-elemental quantification tool for fish feed is determined. A particular focus of this paper is total chromium, an essential element that has the potential to be toxic and carcinogenic. In total six elements, four macro-elements (Ca, Fe, K and Mg) and two micro-elements (Cr and Rb), were modelled using LIBS spectra of aquafeed samples. Reference analysis was conducted via inductively coupled plasma mass spectrometry (ICP-MS) and showed good agreement with LIBS predictions. These results provide evidence that LIBS has the potential to be utilized in the field as a real-time screening tool for establishing the elemental composition of a range of fish feeds.

1. Introduction

Fish and fish products are considered a valuable part of the human diet; containing a good balance of minerals, proteins and vitamins. Historically, fish were consumed as wild catch. However, increases in the human population and a decline in wild fish stocks, associated with over-harvesting and water pollution, have led to a global trend in aquaculture as a solution to satisfy demand. This growth is supported through developments in fish feed production, a key component of any aquaculture system, both from a manufacturing and regulatory point of view. Elemental analysis of both salutary and deleterious elements such as trace elements in feed should be an essential part of any quality management system for fish farms. For example, in countries such as Bangladesh, with substantial tanning industries, chromium entering the food chain via feed is of particular concern [1–3].

A literature review highlights the popularity of spectroscopic techniques and mass spectrometry as a means of determining the elemental composition of fish feed. Simultaneous electrothermal atomic absorption spectrometry (SIMAAS) was used to determine As, Cd, Cu and Pb levels in fish feed [4]. Fish feed samples from the south-western region of Bangladesh have been assessed for trace element (As, Cd, Cr, Hg and Pb) contamination by AAS (atomic absorption spectrometry) [5]. Souza et al. [6] evaluated the following elements Al, B, Ca, Fe, K, Mg, Mn, Na, S, P and Zn by ICP-OES (inductively coupled plasma-optical emission spectrometry); as well as As, Ba, Cd, Cr, Cu, Ni, Pb, Sb, Se, Sr and V in fish feed by ICP-MS (inductively coupled plasma-mass spectrometry). Also, instrumental neutron activation analysis (INAA) has been used to

estimate Ca, Cu, Fe, Mg, Mn, Na, P, and Zn in fish feed [7]. These established techniques are very sensitive and accurate; however in the case of AAS and ICP methods extensive sample preparation such as dissolution and digestion is required. Pressurized gas is also a feature of AAS and ICP approaches while INAA requires a reactor core thus limiting their potential as an at-line production or in-field tool.

In the last decade, there has been a growing interest in the elemental analysis of food products by laser-induced breakdown spectroscopy (LIBS). This technique typically requires little to no sample preparation, is rapid and can be operated without the need for gases. Such features make it a potential technique for in-field testing or as a Process Analytical Technology. Its potential at mapping elemental spatial distributions has also been demonstrated [8,9].

LIBS has been demonstrated for mineral analysis of a wide variety of organic matrices. Gondal et al. [10] analysed Br, Ca, Cu, Fe, K and Si in tea. While Baskali-Bouregaa et al. [11] identified tea geographical origin using LIBS elemental fingerprinting associate with ICP-MS measurement. In another study, Dixit et al. [12] determined Rb levels in beef samples. LIBS has accurately predicted ash levels as well as quantified Mg and K contents in gluten free powders [13]. Trace elements such as Cd and Pb have been determined in rice [14] as well as Cr in rice leaves [15].

This study examines the potential of LIBS as a rapid elemental analysis approach for fish feed. A 150 mJ LIBS system, in combination with chemometric techniques, was used to model six elements (i.e. four macro-elements: Ca, Fe, K and Mg and two micro-elements: Cr and Rb) in a variety of fish feed samples sourced from Bangladesh. Also, the

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ability of LIBS as a method for visualizing sample homogeneity/heterogeneity is displayed via chemical maps.

2. Materials and methods

2.1. Sample material and preparation

Commercial fish feed powder samples were obtained from several aquafeeds manufacturers in Bangladesh. A total of eight different types of dry feed in powder form, suitable for freshwater fish, were used in this study. The product manufacturers state that the feed is suitable for the following fish and their developmental stages: carp starter, carp grower, pangus grower, pangus finisher, telapia nursery, telapia starter, general fish feed powder I and general fish feed powder II.

In order to test the quantitative and qualitative capabilities of LIBS, samples were divided into a calibration set for quantitative analysis and a qualitative set for fingerprint discrimination. The quality of the pellet's mechanical strength can be improved by the addition of a binder. Binders are mainly composed of hydrogen and carbon ensuring minimum interference with the main elements in a spectrum [16]. Five mixtures with different proportion of binder (3644-Ultrabind, Spex, UK) and aquafeed (general fish feed powder II) containing 0%, 20%, 40%, 60% and 80% of fish feed content ($w w^{-1}$) were prepared as quantitative set.

The seven remaining aquafeeds correspond to the qualitative set. For these seven types of feed a 40:60 ratio ($w w^{-1}$) mixture of binder to aquafeed were prepared. All sample mixtures were precisely weighed (500 ± 10 mg) having been prepared in triplicates by adding 200 mg of binder and 300 mg of fish feed into a plastic tube which was then manually shaken and subsequently vortexed. Mixtures are then transferred into a 13 mm diameter stainless steel die and pelleted using a hydraulic press (GS01160, Specac Ltd., Orpington, UK) by applying a pressure of 10 tonnes for 3 min.

In addition, to illustrate LIBS's ability to detect spatial features two heterogeneous pellets were prepared following the previous procedure. The two pellets of approximately 500 mg, were heterogeneously prepared with one side of the pellet composed of 100% binder and the other side a 80:20 ratio ($w w^{-1}$) of binder to aquafeed. The second pellet consisted of a 100% binder on one side and a 40:60 ratio ($w w^{-1}$) of binder to aquafeed on the other side.

In summary, 15 pellets (5 mixtures in triplicates) were employed for quantification, 21 pellets (7 aquafeeds in triplicates) for qualitative analysis and 2 pellets for chemical mapping.

2.2. Reference method

2.2.1. Microwave assisted digestion and sample preparation

For the analysis, 500 mg of sample was transferred to a microwave digestion tube. Thereafter, 10 ml of nitric acid (69%, Sigma Aldrich) was added and left to stand for 15 min. The digestion tubes were screw capped and set in a microwave digester to complete digestion (CEM Corp. MARS 6, Matthews, NC, USA). The microwave digestion settings were temperature: 210 °C, pressure: 800 psi, power: 1000-1800 w, ramp time: 20–25 min and hold time: 15 min. After complete digestion and cooling, the resultant solutions were transferred to plastic, metal-free, 100 ml volumetric flask and ultra-pure deionized water was added until the volume mark was reached. Blank samples and certified reference material (CRM) – Non-Fat Milk Powder (ERM-BD151) - were processed with unknown samples. Aqueous calibration standard solutions were prepared by dilution of the multi-element calibration standard-2A (Agilent Technologies, Japan). For Ca, Mg, K and Fe analysis, the samples required further dilution by a factor of one hundred in order to fit within the calibration range of the reference method. The entire procedure was replicated for each fish feed sample.

2.2.2. ICP-MS instrumentation

Inductively coupled plasma mass spectrometry (ICP-MS) with an octopole reaction system (ORS) was used for the elemental analysis of all fish feed samples (7900 ICP-MS, Agilent, Japan). The plasma was generated via argon gas (purity of 99.9999%) using a plasma flow rate of 15 L min^{-1} , the auxiliary and nebuliser gas both had a flow rate of 1 L min^{-1} . The induction coil was operated at a radio-frequency of 27 MHz with a power of 1.5 kW. The ORS was operated using He (collision mode) with a gas flow rate of 5 ml min^{-1} .

In this work, all reagents used were of analytical grade. Ultra-pure deionized water (resistivity of 18.2 $\text{m}\Omega \text{cm}^{-1}$) was generated in-house (Adrona B30/Integrity+, Riga, Latvia). Prior to use, all vessels used were decontaminated in a nitric acid solution (10% v v^{-1}) for 24 h [17,18] after which they were washed with ultra-pure deionized water three times and dried in an electric oven at 45 °C.

2.3. LIBS instrumentation and measurement

2.3.1. Instrument set-up

LIBS experiments were performed using a LIBS-6 system (Applied Photonics Ltd., Skipton, UK) which is constituted of a 150 mJ Q-switched Nd:YAG laser (Nano SG 150–10, Litron lasers Ltd., Rugby, UK) operating at 1064 nm wavelength with a pulse duration of 5 ns and a repetition rate of 1 Hz coupled with six spectrometers (AvaSpec, Avantes BV, Apeldoorn, Netherlands) covering the spectral range of 181–904 nm. Plasma emission was recorded at a 1.27 μs delay time with an integration time of 1.1 ms.

2.3.2. Measurement

For each pellet, spectra were recorded 3 consecutive times at 100 different spatial locations, following a 10 x 10 grid pattern with an approximately 0.7 mm inter-measurement distance using a motorised X-Y-Z sample chamber (XYZ-750, Applied Photonics Limited, Skipton North Yorkshire, United Kingdom) at the optimum focal length of approximately 80 mm. Measurements were conducted operating the laser in a continuous mode.

2.4. Chemometric analysis

Multivariate analysis was performed using R [19] and the “pls” package [20] for PLSR (partial least square regression) modelling, PCA (Principal Component Analysis) for qualitative analysis along with other in-house functions for quantitative analysis.

In order to correct non-linearities and signals variation introduced by fluctuations in the laser pulse energy and matrix effects, the spectral data was initially pre-processed. Firstly, data collected for each pellet were baseline corrected followed by spectral normalization against the H I atomic spectral line (656.24 nm). This transformation is a standard score calculation for each point of the signal in order to normalise any variation between point measurements within replicates.

For qualitative analysis, PCA was applied to data chosen for fingerprint discrimination in order to reduce the dimensionality of the dataset while retaining as much of the variation present as possible [21].

For quantitative analysis, the median of the 100 locations of the calibration set was used to obtain a single spectrum per analysed pellet. In this study, the use of the median has been preferred to the average, as the median is less affected by outliers. The spectral range where the main spectral line emissions relating to Ca, Cr, Fe, Mg, K and Rb occur was chosen to build six different PLSR models. PLSR is a multivariate technique which develops a linear regression model by projecting the predicted (spectral data) and observed variables (elemental chemical analysis) to a new space to which X-predicted and Y-observed data are transferred [22]. Processed data acquired for the calibration set containing 0%, 40% and 80% fish feed ($n = 9$) were used to develop the calibration model, along with their elemental chemical analysis values

Table 1

Reference analysis (ICP-MS) contents for both macro-elements (Ca, Fe, K and Mg) and micro-elements (Cr and Rb) of eight aquafeeds.

Sample	Ca (mg g ⁻¹) ^a	Fe (mg g ⁻¹) ^a	K (mg g ⁻¹) ^a	Mg (mg g ⁻¹) ^a	Cr (µg g ⁻¹) ^a	Rb (µg g ⁻¹) ^a
Carp starter	3.13 ± 0.16	0.33 ± 0.11	10.2 ± 0.3	4.88 ± 0.16	7.77 ± 0.22	30.2 ± 0.8
Carp grower	2.20 ± 0.06	0.59 ± 0.15	8.16 ± 0.15	5.62 ± 0.11	8.57 ± 0.63	29.3 ± 0.3
Pangus grower	2.25 ± 0.06	0.19 ± 0.09	8.14 ± 0.24	6.03 ± 0.15	7.29 ± 0.30	33.3 ± 1.2
Pangus finisher	1.06 ± 0.03	0.49 ± 0.00	8.41 ± 0.13	5.00 ± 0.08	2.88 ± 0.06	39.6 ± 0.4
Telapia nursery	2.98 ± 0.37	0.49 ± 0.06	10.5 ± 1.0	2.17 ± 0.28	1.27 ± 0.30	15.1 ± 1.4
Telapia starter	16.3 ± 0.4	0.36 ± 0.00	137 ± 2	9.97 ± 0.10	3.72 ± 0.30	25.5 ± 0.9
General fish feed powder I	1.93 ± 0.13	0.66 ± 0.19	10.7 ± 0.5	5.95 ± 0.29	1.48 ± 0.11	17.5 ± 0.7
General fish feed powder II	4.61 ± 0.23	0.54 ± 0.18	11.2 ± 0.4	3.37 ± 0.13	103 ± 5	36.4 ± 1.4

^a mean ± standard deviation (n = 3).

extracted from ICP-MS analysis. The remaining data of the calibration set containing 20% and 60% fish feed (n = 6), along with their elemental chemical analysis values, were used as the validation sample set. The method of leave-one-out was used for cross validation in order to avoid either over- or under-fitting of the models. The calibration model was evaluated by determining the optimum number of components based on the root mean square error in cross validation (RMSECV) and coefficient of determination in cross validation (R_{cv}^2). The prediction accuracy of the developed calibration model was evaluated by calculating the root mean square error of prediction (RMSEP) and the corresponding coefficients of determination in prediction (R_p^2).

3. Results and discussion

3.1. Reference ICP-MS analysis

These elemental results are expressed as mg g⁻¹ for Ca, Fe, K and Mg and as µg g⁻¹ for Cr and Rb (Table 1). Note, as the binder did not contain any detectable levels of these elements, it is omitted from Table 1. The elemental concentrations found in the eight fish feed samples were in the following descending order: K > Ca > Mg > Fe > Cr > Rb. As expected, the four macro-elements (Ca, Fe, K and Mg) are present in higher concentrations than the two micro-elements (Cr and Rb). The aquafeeds contained levels of chromium between 1 and 9 µg g⁻¹, except for one sample, general fish feed II, which contained more than 100 µg g⁻¹. Due to its higher Cr content as measured with the reference ICP-MS analysis, the general fish feed powder II was selected as the calibration aquafeed sample for mineral quantification purposes with LIBS.

3.2. Qualitative set

3.2.1. Spectral analysis and PCA

LIBS spectra of four different aquafeeds samples (carp starter, pangus finisher, telapia nursery and general fish feed powder I), selected randomly, are presented to illustrate the qualitative potential of LIBS. Fig. 1 A. shows the baseline corrected and normalised spectra, representing the median value of 100 locations for one replicate, picked randomly. The spectral lines were associated with the most probable elements emitting at the observed wavelengths, using the spectral lines provided by the NIST database as a reference [23].

In Fig. 1 A., for all samples, the strongest intensities were observed at 589.05 nm and 589.59 nm (both atomic lines) which are generally associated with sodium. Followed by the doublet peak (766.46 nm and 769.93 nm, both atomic lines) of potassium, the multiple peaks at 393.39 nm (ionic line), 396.86 nm (ionic line), 422.65 nm (atomic line) and 616.28 nm (atomic line) attributed to calcium, the peaks at 279.56 nm (ionic line) and 518.40 nm (atomic line) of magnesium and finally those at 438.30 nm and 526.96 nm (both atomic lines) associated with iron. It is interesting to note that this decreasing order in the macro-elements intensity (K, Ca, Mg and Fe) broadly matches the elemental concentration decreasing order as measured by ICP-MS

(Table 1). Concerning the micro-elements, chromium is associated with the wavelength 520.83 nm (atomic line), and rubidium at 780.01 nm (atomic line) these could be seen in most samples. For all samples, atomic emission line of hydrogen at 656.24 nm, nitrogen at 742.41 nm, 744.28 nm and 746.91 nm, together with oxygen at 777.43 nm could be observed; it is worth noting that all experiments involving LIBS were conducted under normal atmospheric conditions (i.e. no purge gases) [24].

Each aquafeed spectrum presented had a unique pattern (Fig. 1 A.). Indeed, whatever the element observed the general fish feed powder I presented the highest intensities. For Na, Ca, Mg, Fe and Cr the sample's decreasing order of intensities are similar i.e. carp grower, telapia nursery and pangus finisher while for K it is telapia nursery first then carp starter and finally pangus finisher. Ideally, the LIBS measurements would always match the chemical concentration ordering of the ICP-MS analysis. However, LIBS can be affected by factors including; self-absorption and matrix effects, leading to emission line intensities no longer proportional to the concentration of the element in the plasma. In order to summarise the structure of the data in a lower dimensional space a PCA was applied on the entire LIBS spectra (only baseline corrected) of 4 aquafeeds (carp starter, pangus finisher, telapia nursery and general fish feed powder I). The resulting PCA score plot of the first two principal components (PC) is depicted in Fig. 2. PC1 and PC2 accounted respectively for 16.6% and 4.6% of the total variance. The four previously defined types of aquafeeds, enclosed by their respective 95% confidences, can be distinguished principally by PC1. Pangus finisher samples are on left of the figure, while general fish feed powder I samples plot on the right side. Telapia nursery and carp starter samples lie between the two other groups (Fig. 2).

In agreement with Fig. 1 A., samples with similar spectral patterns show clusters with a slight overlap, such as carp starter and telapia nursery. On the other hand, samples with different spectral patterns between samples (Fig. 1 A.), and therefore elemental composition, show distinct clusters such as pangus finisher and general fish feed powder I, where in Fig. 2, a clear separation can be seen. This is consistent with the PCA loading plot data (Fig. i) in supplementary information.

3.3. Quantitative set

3.3.1. LIBS spectral analysis

For clarification, the median LIBS spectra obtained from three different samples: 100% binder, 40% general fish feed powder II (60% binder) and 80% general fish feed powder II (20% binder) are presented in Fig. 3. A clear increase in the intensity of Cr (520.83 nm), Ca (393.39 nm, 422.65 nm and 643.93 nm), Mg (279.56 nm and 518.40 nm), K (766.46 nm and 769.93 nm), Fe (526.96 nm) and Rb (780.01 nm) emission lines for samples with an increasing amount of feed content can be observed. Indeed, whatever the element, the maximum intensities were observed for the 80% feed sample (Fig. 1 B.c) while the lowest intensities or no peaks are observed for the 100% binder (Fig. 1 B.a), i.e. 0% feed. These results are promising for the use

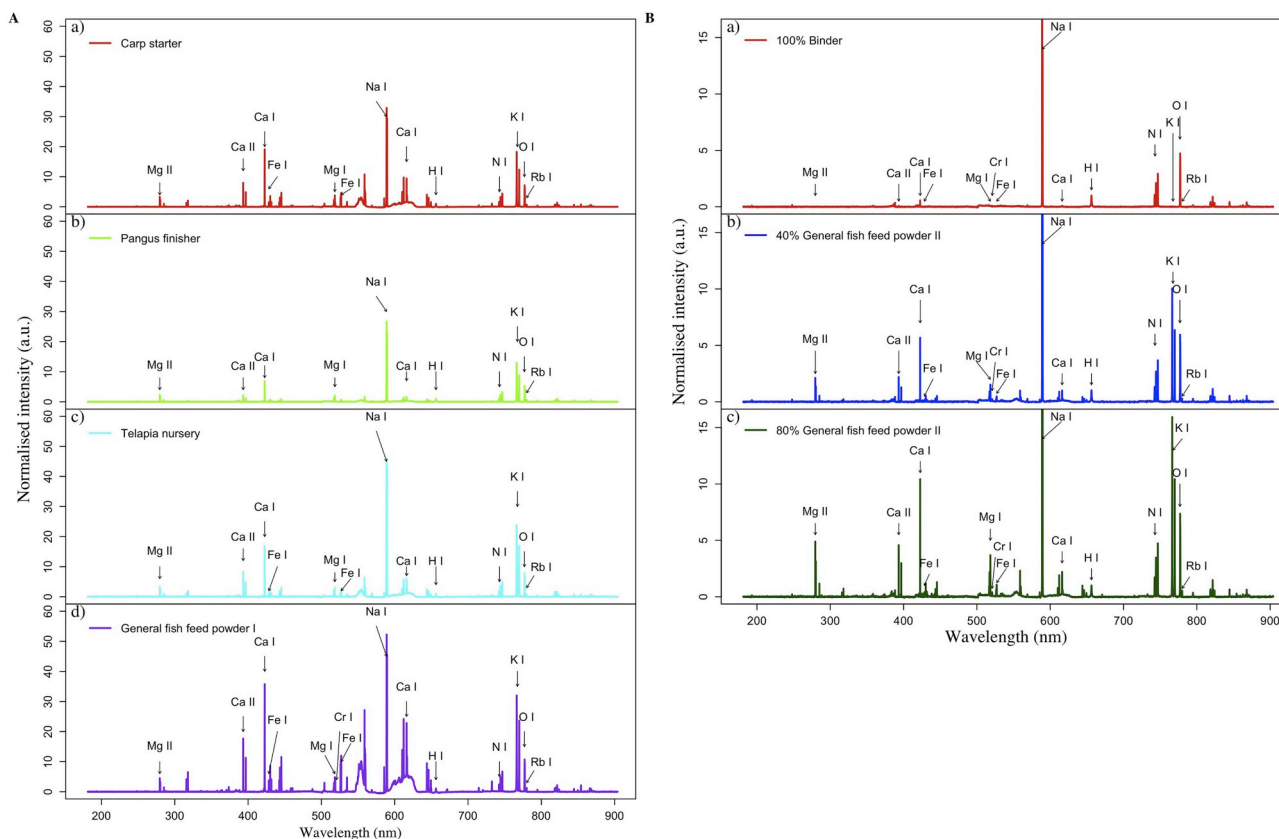


Fig. 1. Median LIBS spectra of A. 4 different aquafeeds: a) Carp starter, b) Pangus finisher, c) Telapia nursery and d) General fish feed powder I. B. 3 mixtures with different proportion of binder and aquafeed: a) 100% Binder, b) 40% General fish feed powder II, c) 80% General fish feed powder II. Spectra are vertically offset for clarity. The Roman numeral “I” refers to the neutral atom and “II” to the singly-ionized state of the chemical element.

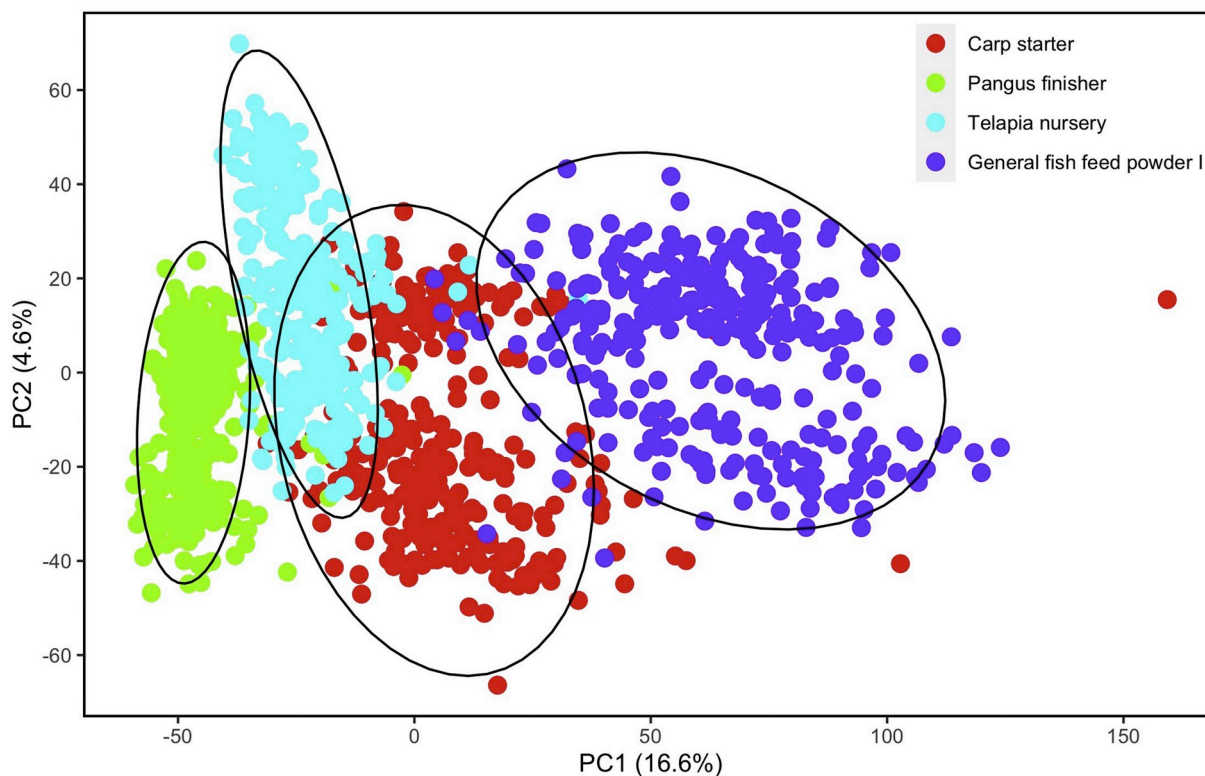


Fig. 2. Score plot of PC1 vs PC2 of a principal component analysis on LIBS spectra of 4 different aquafeeds (carp starter, pangus finisher, telapia nursery and general fish feed powder I) with their 95% confidence ellipses.

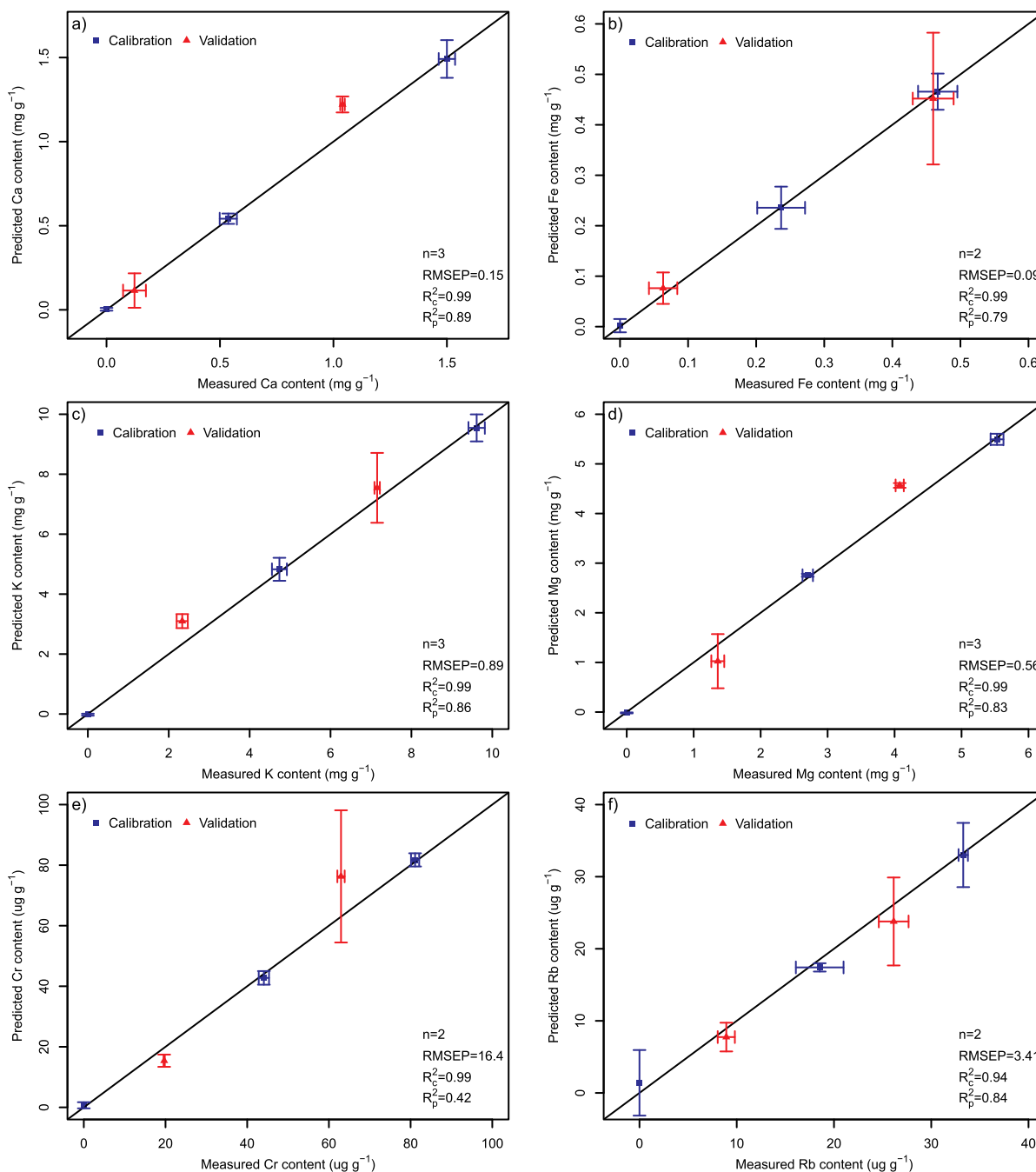


Fig. 3. PLS calibration and validation models of: a) calcium content, b) iron content, c) potassium content, d) magnesium content, e) chromium content and f) rubidium content in general fish feed powder II.

of LIBS in quantitative analysis of aquafeed.

3.3.1. Calibration and validation models

Calibration models were constructed using PLS regression performed on a calibration data set (100% binder, 40% feed and 80% feed). The concentrations determined by ICP-MS were utilized as observed variables for PLSR, thus relating elements (Ca, Cr, Fe, K, Mg and Rb) to pre-processed LIBS spectra data. As mentioned above, the full pre-processed LIBS spectra data were not used but wavelength range specific to each element of interest such as 460.46 nm–460.92 nm and 519.55 nm–522.11 nm for Cr. A key parameter in the construction of a robust, neither over- nor under-fitted model, is the selection of the optimum numbers of PLS factors. Indeed, too many factors may lead to

an unstable model which over-fits the data implying a random noise instead of the link between observations and predictions. Conversely, too few factors may lead to an under-fitted model integrating inadequate information of data [25]. Cross-validated (CV) prediction using the leave-one-out method was applied in this study to increase the model accuracy and determine the optimum number of latent variables based at the same time on a low root mean square error of CV (RMSECV) and a high R_{cv}^2 . Table 2 summarized the performance of the calibration model: number of PLS factors, coefficients of determination and root mean square errors for calibration (R_c^2 , RMSEC), cross-validation (R_{cv}^2 , RMSECV) and prediction (R_p^2 , RMSEP) by an independent data set. The optimum number of PLS factors is 3 for Ca, K and Mg while it is 2 for Fe, Cr and Rb (Table 2). Moreover, as displayed in

Table 2
Calibration Cross-validation and prediction performance parameters of PLSR models using LIBS.

Element	No. PLS factors	Calibration (n=9)		Cross-validation		Validation (n=6)	
		R_c^2	RMSEC ^a	R_{cv}^2	RMSECV ^a	R_p^2	RMSEP ^a
Ca	3	0.99	0.06	0.90	0.19	0.89	0.15
Fe	2	0.99	0.01	0.94	0.04	0.79	0.09
K	3	0.99	0.30	0.94	0.94	0.86	0.89
Mg	3	0.99	0.13	0.97	0.36	0.83	0.56
Cr	2	0.99	1.34	0.99	2.87	0.42	16.4
Rb	2	0.94	3.36	0.71	7.34	0.84	3.41

^a Expressed in milligrams per gram for macro-elements (Ca, Fe, K and Mg) and micrograms per gram for micro-elements (Cr and Rb).

Fig. 3, which shows the scatter plot of the measured and predicted content of element of interest, a good linearity of the model whatever the element could be showed. Table 2 and Fig. 3 show a R_c^2 for most of the elements equal to 0.99 (except of Rb 0.94) and R_{cv}^2 , higher than 0.90 (except of Rb 0.71). The slightly decreased values between the calibration and cross-validation root square (R_c^2 and R_{cv}^2 respectively) and the slight increase between RMSEC and RMSECV point to models that are not over fitted.

The robustness of calibration models was assessed by applying the 6 models on the validation data set. Fig. 3 shows a good prediction for all elements with both RMSEP and RMSECV values similar, indicating a robust model.

Lower correlation for Cr (R_p^2) and higher RMSEP compared to other elements presented in this study is probably due to the low Cr content in fish feed and the fact that natural material, even finely crushed remains heterogeneous. More replicates and/or more samples could improve prediction model.

According to these results, it can be concluded that the prediction models have a good performance in predicting Ca, Fe, K, Mg, Cr and Rb in aquafeeds.

3.3.2. Chemical maps

In order to study the Cr distribution within a sample, an intensity map displaying the 100 locations analysed per sample at 520.83 nm is presented in Fig. 4. Fig. 4 (a)–(e) show the intensity distribution of Cr at 520.83 nm of the calibration set from 100% binder content (Fig. 4a) to 80% general fish feed powder II content (Fig. 4e). An obvious distinction between different mixtures of feed percentages is viewed based on their Cr line intensity, indicated by the colour scale from dark blue for low intensities to dark red/brown for high intensities. Indeed in the binder, where there is no chromium the pellet is represented as a completely dark blue matrix (Fig. 4a), whereas the 80% fish feed is dark red/brown (Fig. 4e) and in between samples a colour scale explaining proportionate concentrations. These spatial distribution maps demonstrate that the intensity of Cr is directly proportional to the feed content.

To further explain the spatial distribution capabilities of LIBS, two supplementary pellets containing two different mixtures of the feed content were analysed. Fig. 4 (f) and Fig. 4 (g) represent the Cr intensity distribution in 2 pellets containing on one side with 100% binder and their corresponding half a 80:20 ratio ($w w^{-1}$) and 40:60 ratio ($w w^{-1}$) of binder to general fish feed powder II. For both pellets, a colour scale could be observed from the 100% binder side, which is a dark blue, and the mixture of binder and aquafeed, which is light blue for 80:20 mixture and blue-green with orange spot in the 40:60 mixture. These two figures (Fig. 4 f and g) also demonstrate that LIBS can spatially distinguish chromium (Cr) intensity within the pellet.

4. Conclusion

The present work demonstrates the feasibility of LIBS combined with chemometric techniques as a rapid analytical technique for qualitative and quantitative analysis of calcium, chromium, iron, magnesium, potassium and rubidium content in different types of fish feed samples. The main advantages of LIBS technique compared to reference methods for element content determination are its rapidness, user-friendliness and minimal sample preparation. PLS regression for each

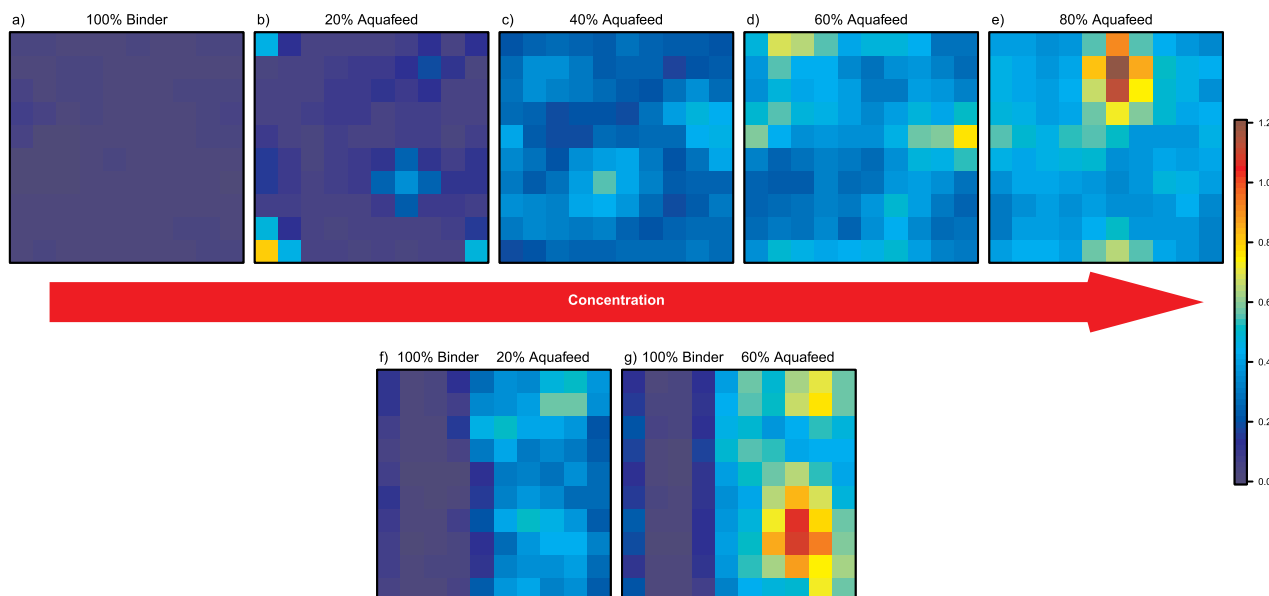


Fig. 4. Intensity mapping distribution at emission line 520.83 nm for single pellets of: a) 100% binder, b) 20% general fish feed powder II, c) 40% general fish feed powder II, d) 60% general fish feed powder II and e) 80% general fish feed powder II. f) Two different mineral concentrations arranged side by side, containing from left to right: 100% binder and 20% general fish feed powder II and g) two different mineral concentrations arranged side by side, containing from left to right: 100% Binder and 60% general fish feed powder II. The colour scale indicates the baseline corrected and normalised intensity. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

element was performed to build a model allowing their quantification in aquafeeds. The results illustrate that LIBS offers the potential to detect and quantify minerals in fish feed, offering potential for real-time monitoring of elemental composition. Moreover, the chemical cartography conducted in this study allows a better understanding of chromium distribution within samples. The findings illustrate the ability of LIBS to identify not only the chemical composition of feed samples but also the spatial elemental distribution.

The technology has the potential to offer in-field or process analysis of fish feed. However, further studies are required to identify other elements, strengthen the models and make LIBS a suitable technique for routine analysis in an industrial environment.

Author agreement statement

We the undersigned declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere. We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us. We understand that the Corresponding Author is the sole contact for the Editorial process. He is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2020.121258>.

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