

Evaluation of the Mineral Contents in Fish Meal by FT–NIR using PLS and Kernel PLS

S. MASOUM^{1,*}, A. ALISHAHI², M. SHEKARCHI³ AND H. FARAHMAND²

¹*Department of Analytical Chemistry, Faculty of Chemistry, University of Kashan, Kashan, I. R. IRAN*

²*Department of Fisheries and Environmental Science, Tehran University, Karaj, IRAN*

³*Laboratory of Food and Drug, Sanitary Ministry of Iran, Tehran, IRAN*

(Received May 1, 2011)

ABSTRACT

In the present work we study the use of Fourier transform near infrared spectroscopy (FT-NIRS) technique to analysis the calcium (Ca), phosphorus (P) and copper (Cu) contents of fish meal. The regression methods employed were partial least squares (PLS) and kernel partial least squares (KPLS). The results showed that the efficiency of KPLS was better than PLS. As a whole, the application of FT-NIRS with PLS and KPLS was as a suitable option for replacing the routine chemical analysis to assess the mineral content in fish meal, allowing immediate control of the fish meal without prior sample treatment or destruction.

Keywords: Calcium, Phosphorus, Copper, Fish meal, FT-NIRS, KPLS

1 INTRODUCTION

Fish meal industry plays an important role directly or indirectly in the nutrition and food quality for human nutrition. Fish meal is abundantly used in formulating the diets for animal which mostly is due to high level content of protein. The protein content of fish meal have several privileges in respect to the other portentous sources including high digestibility, palatability, amino acid balance, low level of anti nutritional compounds and unknown growth factor [1]. As a whole, fish meal is one of the most important ingredients in formulated aqua feeds, and particularly in shrimp feeds because shrimp and crustaceans need high content of protein with suitable digestibility and balanced amino acids that fish meal from this view is excellent [2].

*Corresponding Author (Email: masoum@kashanu.ac.ir).

Fish meal is composed from various compositions including protein, fat (particularly polyunsaturated fatty acids), pigments, vitamins and minerals, which are essential for the functioning of living beings, although the amounts supplied to animals must be present in the correct proportions since, on the one hand, deficiencies in these essential components lead to diseases such as anemia, disorder in the functioning of enzymes, disturbance in the absorption of nutrients in intestine, incorrect operation of reproductive apparatus (organs), decrease in the immunity of defense system of the body, delays in growth, etc., while on the other hand their excess consumption brings about intoxication, the accumulation of such compounds in the organism, auto-oxidation of fat, immunosuppression effect and the other malfunctioning. Thus the importance of these essential compounds in the diet is the same as the suitable amounts of the nutrient and generally the best formulation of the diet for the target organism ultimately causing safety and health of reared animals [3]. Many elements, which are present in seafood [4] are indispensable for human health only at low concentration [5], however, they can be toxic at high concentration [4, 5].

The ash (mineral) content of fish meal can range from 10 to 25%. Fish meal is an excellent source of calcium, phosphorus and copper for animal feeding. The copper content in fish meal is crucial from point of view of pollution index because in the contaminated realms, the accumulation of copper in the tissue increases which this phenomenon is so-called bioaccumulation. Thus it is obvious that copper content in addition of nutritional value, has an important role in pollution index. As a whole, mineral (ash) content in fish meal affirms the origin of fish or aquatic organism to produce the fish meal. For example, mineral content of the fish meal produced by whole fish is less than that produced by by-catch or fish and crustacean leftover [6]. The higher ash content is usually an indication of a higher calcium, phosphorus and copper level. The calcium, phosphorus and copper are in a highly available form, unlike some of calcium, phosphorus and copper in plants protein that bioavailability of the essential nutrients is more critical than the amounts of the nutrients in diet [7].

The partial least squares (PLS) method has been a popular modeling, regression, discrimination and classification technique in its domain of origin-chemometrics. In its general form, PLS creates score vectors (components, latent vectors) by using the existing correlations between different sets of variables (blocks of data) while also keeping most of the variance of both sets. PLS has proven to be useful in situations where the number of observed variables is much greater than the number of observations and high multicollinearity among the variables exists. Kernel PLS (KPLS) differs from the nonlinear PLS algorithms in that the original input data are nonlinearly transformed into a feature space of arbitrary dimensionality via nonlinear mapping, and then a linear PLS model is created in the feature space. KPLS can efficiently compute regression coefficients in high-dimensional feature spaces using nonlinear kernel functions. Compared to other nonlinear

approaches, the main advantage of KPLS is that it avoids nonlinear optimization by utilizing the kernel function corresponding to the inner product in the feature space, F [8].

The aim of the present work was to explore the potential and accuracy of FT-NIR for predictions of Ca, P, and Cu in fish meal without prior sample treatment, using direct application of the NIR.

2. EXPERIMENTAL

2.1. FT-NIR Spectroscopy

A FT-NIR Systems (Bomem, 450 St-Iean Baptiste, Quebec PQ Canada G2E 5S5, Version 1, 1994) fitted for the spectrum analysis. Samples were collected from the plants in north and south of Iran. Near infrared spectra (1000-2500nm) of whole fish meal were scanned in triplicate with the Bomem M & MB. The sample was filled into standard Petri dishes. The measurement cell used is the beaker, which measures samples in Reflection. Each sample was scanned 64 times and the data obtained was averaged. The software used was Bomem-GRAMS/32 which has been installed on the Pentium III computer.

All computations and chemometric analyses were executed with programs in Matlab v7.2 (The Mathworks, Inc., Natick, MA, USA). All calculations were performed on a 3.40 GHz Pentium IV with 1 GB of RAM.

3. THEORY

3.1. Partial Least Squares (PLS)

PLS was originally developed to achieve two main objectives: to approximate \mathbf{X} and \mathbf{Y} accurately, and to model the relationship between \mathbf{X} and \mathbf{Y} [9]. Details on the PLS algorithms can be found in Ref. [10].

PLS regression is a technique for modeling a linear relation between two data sets (blocks of observed variables). Denote by $\mathbf{x} \in \mathbf{R}^N$ an N -dimensional vector of variables in the first block of data and similarly $\mathbf{y} \in \mathbf{R}^M$ denotes a vector of variables from the second set. PLS models the relations between these two blocks by means of latent variables. Observing n data samples from each block of variables, PLS decomposes the $(n \times N)$ matrix of zero mean variables \mathbf{X} and the $(n \times M)$ matrix of zero mean variables \mathbf{Y} into the form

$$\mathbf{X} = \mathbf{TP}^T + \mathbf{F} \quad (1)$$

$$\mathbf{Y} = \mathbf{UQ}^T + \mathbf{G} \quad (2)$$

where the \mathbf{T} , \mathbf{U} are $(n \times p)$ matrices of the extracted p score vectors (components, latent vectors), the $(N \times p)$ matrix \mathbf{P} and the $(M \times p)$ matrix \mathbf{Q} represent matrices of loadings and the $(n \times N)$ matrix \mathbf{F} and the $(n \times M)$ matrix \mathbf{G} are the matrices of residuals.

The PLS regression model can be expressed with regression coefficient \mathbf{B} and residual matrix \mathbf{R} as follows:

$$\mathbf{Y} = \mathbf{X}\mathbf{B} + \mathbf{R} \quad (3)$$

$$\mathbf{B} = \mathbf{W}(\mathbf{P}^T\mathbf{W})^{-1}\mathbf{C}^T \quad (4)$$

where \mathbf{P} $(N \times k)$ is the matrix consisting of loading vectors $\mathbf{p}_i = \mathbf{X}^T \mathbf{t}_i / (\mathbf{t}_i^T \mathbf{t}_i)$ $i = 1, \dots, k$.

Due to the fact that $\mathbf{p}_i^T \mathbf{w}_j = 0$ for $i > j$ and in general $\mathbf{p}_i^T \mathbf{w}_j \neq 0$ for $i < j$, the matrix $\mathbf{P}^T\mathbf{W}$ is upper triangular and thus invertible [11]. Moreover, using the fact that $\mathbf{t}_i^T \mathbf{t}_j = 0$ for $i \neq j$ and $\mathbf{t}_i^T \mathbf{u}_j = 0$ for $j > i$, Rännar et al. [12] derived the following equalities:

$$\mathbf{W} = \mathbf{X}^T \mathbf{U} \quad (5)$$

$$\mathbf{P} = \mathbf{X}^T \mathbf{T} (\mathbf{T}^T \mathbf{T})^{-1} \quad (6)$$

$$\mathbf{C} = \mathbf{Y}^T \mathbf{T} (\mathbf{T}^T \mathbf{T})^{-1} \quad (7)$$

Substituting Eqs. (5)–(7) into Eq. (4) using the orthogonality of the matrix \mathbf{T} columns, we can write the matrix \mathbf{B} in the following form:

$$\mathbf{B} = \mathbf{X}^T \mathbf{U} (\mathbf{T}^T \mathbf{X} \mathbf{X}^T \mathbf{U})^{-1} \mathbf{T}^T \mathbf{Y} \quad (8)$$

which will be used to make predictions in PLS regression.

3.2. Kernel Partial Least Squares (KPLS)

In kernel PLS regression a linear PLS regression model in a feature space F is considered. KPLS is formulated in this feature space to extend linear PLS to its nonlinear kernel form.

First, consider a nonlinear transformation of the input variables x_i , $i = 1, \dots, n$ into feature space F : $\mathbf{X}_i \in \mathbf{R}^N \rightarrow \Phi(\mathbf{x}_i) \in F$ where it is assumed that $\sum_{k=1}^N \Phi(x_k) = 0$, and $\Phi(\cdot)$ is a nonlinear mapping function that projects the input vectors from the input space to F . Note that the dimensionality of the feature space is arbitrarily large, and can even be infinite. Denote Φ as the $(n \times S)$ matrix whose i -th row is the vector $\Phi(\mathbf{x}_i)$ in an S dimensional feature space F . As shown in Table 1, the KPLS algorithm is directly derived from the PLS algorithm by modifying steps 2 and 3 of the PLS procedure so as to use the matrix Φ of mapped input data instead. Through the introduction of the kernel trick, $\Phi(\mathbf{x}_i)^T \Phi(\mathbf{x}_j) = \mathbf{K}(x_i, x_j)$, one can avoid both performing explicit nonlinear mappings and computing dot products in the feature space. Note that $\Phi\Phi^T$ represents the $(n \times n)$ kernel Gram matrix \mathbf{K} of the cross dot products between all mapped input data points $\Phi(\mathbf{x}_i)$, $i = 1, \dots, n$.

The deflation of the $\Phi\Phi^T = \mathbf{K}$ matrix after extraction of the \mathbf{t} component is now given by:

$$\mathbf{K} \leftarrow (\mathbf{I} - \mathbf{t}\mathbf{t}^T) \mathbf{K} (\mathbf{I} - \mathbf{t}\mathbf{t}^T) = \mathbf{K} - \mathbf{t}\mathbf{t}^T \mathbf{K} - \mathbf{K}\mathbf{t}\mathbf{t}^T + \mathbf{t}\mathbf{t}^T \mathbf{K}\mathbf{t}\mathbf{t}^T \quad (9)$$

where I is an n -dimensional identity matrix.

As in Eq. (8), the matrix of the regression coefficient \mathbf{B} in the KPLS algorithm will have the form:

$$\mathbf{B} = \Phi^T \mathbf{U} (\mathbf{T}^T \mathbf{K} \mathbf{U})^{-1} \mathbf{T}^T \mathbf{Y} \quad (10)$$

As a result, when the number of test data is $n_t(1, \dots, n_t)$, the predictions on training data and test data can be made as follows, respectively:

$$\hat{\mathbf{Y}} = \Phi \mathbf{B} = \mathbf{K} \mathbf{U} (\mathbf{T}^T \mathbf{K} \mathbf{U})^{-1} \mathbf{T}^T \mathbf{Y} \quad (11)$$

$$\hat{\mathbf{Y}}_t = \Phi_t \mathbf{B} = \mathbf{K}_t \mathbf{U} (\mathbf{T}^T \mathbf{K} \mathbf{U})^{-1} \mathbf{T}^T \mathbf{Y} \quad (12)$$

Here, Φ_t is the matrix of the mapped test points and is \mathbf{K}_t the $(n_t \times n)$ test matrix whose elements are $\mathbf{K}_{ij} = \mathbf{K}(\mathbf{x}_i, \mathbf{x}_j)$, where \mathbf{x}_i is the i -th test vector and \mathbf{x}_j is the j -th training vector. Before applying KPLS, mean centering in the high dimensional space should be performed. This can be done by substituting the kernel matrices \mathbf{K} and \mathbf{K}_t with $\hat{\mathbf{K}}$ and $\hat{\mathbf{K}}_t$, where

$$\hat{\mathbf{K}} = (\mathbf{I} - \mathbf{I}_n \mathbf{I}_n^T / n) \mathbf{K} (\mathbf{I} - \mathbf{I}_n \mathbf{I}_n^T / n) \quad (13)$$

$$\hat{\mathbf{K}}_t = (\mathbf{K}_t - 1/n \mathbf{1}_{n_t} \mathbf{1}_n^T \mathbf{K}) (\mathbf{I} - 1/n \mathbf{1}_n \mathbf{1}_n^T) \quad (14)$$

Here, \mathbf{I} is an n -dimensional identity matrix and $\mathbf{I}_n, \mathbf{I}_{n_t}$ represent vectors whose elements are ones, with length n and n_t respectively. There exist a number of kernel functions. Representative kernel functions are given below:

Polynomial kernel: $k(\mathbf{x}, \mathbf{y}) = \langle \mathbf{x}, \mathbf{y} \rangle^d$ (15)

Sigmoid kernel: $k(\mathbf{x}, \mathbf{y}) = \tanh(\beta_0 \langle \mathbf{x}, \mathbf{y} \rangle + \beta_1)$ (16)

Radial basis kernel: $k(\mathbf{x}, \mathbf{y}) = \exp(-\|\mathbf{x} - \mathbf{y}\|/c)$ (17)

where $d, \beta_0, \beta_1,$ and c are specified a priori by the user.

Table 1. Comparison of the PLS and KPLS algorithms

PLS	Kernel PLS
1 Randomly initialize \mathbf{u}	Randomly initialize \mathbf{u}
2 $\mathbf{w} = \mathbf{X}^T \mathbf{u}$	$\mathbf{t} = \Phi \Phi^T \mathbf{u} = \mathbf{K} \mathbf{u}$ $\mathbf{t} \leftarrow \mathbf{t} / \ \mathbf{t}\ $
3 $\mathbf{t} = \mathbf{X} \mathbf{w}$ $\mathbf{t} \leftarrow \mathbf{t} / \ \mathbf{t}\ $	
4 $\mathbf{c} = \mathbf{Y}^T \mathbf{t}$	$\mathbf{c} = \mathbf{Y}^T \mathbf{t}$
5 $\mathbf{u} = \mathbf{Y} \mathbf{c}$ $\mathbf{u} \leftarrow \mathbf{u} / \ \mathbf{u}\ $	$\mathbf{u} = \mathbf{Y} \mathbf{c}$ $\mathbf{u} \leftarrow \mathbf{u} / \ \mathbf{u}\ $
6 Repeat steps 2, 3, 4, and 5, until convergence	Repeat steps 2, 3, 4, and 5, until convergence
7 Deflate \mathbf{X}, \mathbf{Y} matrices: $\mathbf{X} \leftarrow \mathbf{X} - \mathbf{t} \mathbf{t}^T \mathbf{X}$ $\mathbf{Y} \leftarrow \mathbf{Y} - \mathbf{t} \mathbf{t}^T \mathbf{Y}$	Deflate \mathbf{K}, \mathbf{Y} matrices: $\mathbf{K} \leftarrow (\mathbf{I} - \mathbf{t} \mathbf{t}^T) \mathbf{K} (\mathbf{I} - \mathbf{t} \mathbf{t}^T)$ $\mathbf{Y} \leftarrow \mathbf{Y} - \mathbf{t} \mathbf{t}^T \mathbf{Y}$

4. RESULTS AND DISCUSSION

Chemical analysis was implemented according to the Martin et al. [3]. The characteristics of reference data were displayed in the Table 2. Of interest in this table are the elevated standard deviations for Ca and P, owing to the variability in the composition of the samples, probably as a consequence of using several fish species during the fish meal processing.

Table 2. Statistical results of chemical analyses (all units in gr/100gr samples)

Components	n	Range	Mean	SD
Ca	120	2.04-4.2	3.03	0.41
P	120	1.0-3.2	2.12	0.47
Cu	120	0.001-0.054	0.025	0.01

To resolve the difficulties of relevance with noises; pre-treatment of the original spectra takes place using from standard normal variates (SNV). The utilization of the SNV method brings about which obviates multiplicative interferences, particle size, the change of light distance and curvilinearity. Also it rectifies multiplicative and additive impacts [13]. The original spectra and their mean cantered spectra and also standard normal variates transform (SNV).

After the pre-treatment of the spectra and increasing their resolution, the next step meaning to build calibration models was implemented to predict the interested components in fish meal. In this research to make the calibration models was used from Kernel Partial Least Square (KPLS). KPLS have more efficient in building the calibration models than PLS because of its non-linearity nature. To obtain suitable calibration models, the samples divided into two groups consisting of training set, monitoring set and validation set. The numbers of samples in the training and monitoring sets were 60 and 35 respectively. The results of multivariate analysis of partial least square (PLS) and kernel partial least square (KPLS) are summarized in Table 3.

As the results showed the precision and efficiency of KPLS was better than PLS that the main reason for these results was the non-linearity nature of KPLS [14]. These results have certificated the former inference about better efficiency and precision of KPLS than PLS. After internal and external validations, the obtained outcomes manifested that the efficiency of KPLS was more than PLS. In KPLS due to its non-linearity nature, factors which achieved between loadings and scores produced high efficient relationship between them. Most overtone regions existed in the range of short wavelengths of near infrared spectroscopy that this point showed it could be used to evaluate the heterogonous portion

especially in the inner sections of fish meal because high power of penetration of spectrum in the low wavelength gives more precise information about the components [15].

Table 3. The results of PLS and KPLS analysis

Components		F ^a	R _T ^b	R _M ^b	RMSE _T ^c	RMSE _M ^c
Ca	PLS	7	0.9127	0.8573	0.1743	0.2246
	KPLS	10	0.9138	0.9024	0.1732	0.2011
P	PLS	6	0.8171	0.8233	0.2735	0.2506
	KPLS	7	0.9404	0.8249	0.1614	0.2577
Cu	PLS	5	0.9049	0.8593	0.0048	0.0057
	KPLS	8	0.9372	0.8521	0.0039	0.0062

^a Number of latent variable

^b Correlation coefficient of training (T) and monitoring (M) sets

^c Root mean of square error of training (T) and monitoring (M) sets

5. CONCLUSIONS

The results of this investigation demonstrate that the application of FT-NIR using multivariate analyses is very beneficial and efficient to assess quantity of Ca, P and Cu in fish meals. The method is easier than routine chemical analyses. This procedure is time consuming and from the cost facets is lucrative.

ACKNOWLEDGMENT. The authors are grateful from Dr. Pirali, the head of the food and drug center in the sanitation ministry of Iran. Also the authors appreciate from the chairman of the environmental and fisheries department and M. Abasi and S. Fekri.

REFERENCES

1. A. Zugarramurdi, M.A. Parin, G.A. Carrizo, L. Gadaleta and H.M. Lupin, Investment and production costs for fishmeal plants in developing and developed countries, *Int. J. Prod. Econ.* **76** (2002), 53-59.
2. A.G.S. Tacon and D. Akiyama, Feed ingredients. In: L. R. D'Abramo, D. E. Conklin, D. M. Akiyama (Eds.), *Crustacean Nutrition: Advances in World Aquaculture*. World Aquaculture Society, Baton Rouge, Louisiana (1997).

3. A.M. Martín, A.V. Alvarez-Garcia, C.G. Perez and V. Garcia, Determination of inorganic elements in animal feeds by NIRS technology and a fibre-optic probe, *Talanta* **69** (2006), 711-715.
4. J. Oehlenschläger, Marine fish – a source for essential elements? In: J.B. Luten, T. Børresen, J. Oehlenschläger (Eds.), *Seafood from producer to consumer, Integrated approach to quality*. Elsevier Science BV, Amsterdam, 1997.
5. S. Fraustro and R.J.P. Willam The biological chemistry of the elements the inorganic chemistry of life. Clarendon Press, Oxford, 1993.
6. Z.E. Sikorski, A. Gildberg and A. Ruitter, *Fish products: fish and fishery products*. CAB International, Wallingford, United Kingdom, 1995.
7. D.M. Richard and J.P. Jacqueline, Methods of the assessment of mineral in feeds. 2003, Web site at <http://edis.ifas.ufl.edu>.
8. R. Rosipal, L.J. Trejo, Kernel partial least squares regression in reproducing Kernel Hilbert space, *J. Mach. Learn. Res.* **2** (2001), 97– 123.
9. K. Kim, J. M. Lee and I. B. Lee, A novel multivariate regression approach based on kernel partial least squares with orthogonal signal correction, *Chemom. Intell. Lab. Syst.* **79** (2005), 22 – 30
10. P. Geladi and B.R. Kowalski, Partial least squares regression: a tutorial, *Anal. Chim. Acta* **185** (1986), 1 –17.
11. A. Höskuldsson, PLS regression methods, *J. Chemom.* **2** (1988), 211– 228.
12. S. Rännar, F. Lindgren, P. Geladi and S.Wold, A PLS kernel algorithm for data sets with many variables and fewer objects. Part 1: theory and algorithm, *J. Chemom.* **8** (1994), 111 – 125.
13. M. Uddin, E. Okazaki, M. Ahmad, Y. Fukuda and M. Tanaka, “NIR spectroscopy: A non-destructive fast technique to verify heat treatment of fish-meat gel”, *Food Control* **17** (2006), 660–664.
14. W. Small, “Chemometrics and near-infrared spectroscopy: Avoiding the pitfalls”, *Trends Anal. Chem.* **11** (2006), 1057-1066.
15. G. Xiccato, A. Trocino, F. Tulli, and E. Tibaldi, “Prediction of chemical composition and origin identification Of European sea bass (*Dicentrarchus labrax* L.) by near infrared reflectance spectroscopy (NIRS)”, *Food Chem.* **86** (2004), 275– 281.