PQS detects adulteration of fishmeal with meat and bone meal—a contribution to help eradicate "Mad Cow Disease"

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Introduction

Having established a link between feeding cattle with ruminant-derived meat and bone meal and the UK epidemic of BSE (bovine spongiform encephalopathy) and its fatal human equivalent, variant CJD (Creutzfeldt–Jakob Disease), it is obligatory that the infective prion is removed from the food chain. Fishmeal, however, is a high value, high quality protein, energy and mineral source for livestock that has never caused disease. Safety concerns about fishmeal as a protein concentrate centre on the risk of contamination or adulteration with meat and bone meal either by accident, ignorance or fraud. The feed industry therefore needs appropriate methods to detect such contamination and deter fraud or malpractice. NIR spectroscopy, as a rapid screening method, can be the first line of defence of the food chain. Murray *et al*.[1] reported that a partial least squares discriminant applied to visible and NIR reflectance spectra successfully detected meat and bone meal in fishmeal. The purpose of our study was to demonstrate the feasibility of using PQS (polar qualification system) as a qualitative evaluation method to identify fishmeal adulterated with land animal proteins at low levels.

Materials and methods

Dry samples packed in quartz cups (55 mm dia.) were scanned in 0–45° reflectance mode as log 1/*R* on a Foss NIRSystems 6500 spectrometer from 400 to 2500 nm at 2 nm intervals. Signal averaging was conducted relative to the instrument reference tile (16–32–16). Spectra consisted of 46 pure, unadulterated fishmeal samples and 90 samples as three groups of 30 specimens each of which were different fishmeals deliberately contaminated with different meat and bone meal to a concentration of 3%, 6% and 9% by weight, respectively. All samples were unique specimens used once only.

The PQS used for evaluation is a powerful data-reduction and qualification method[2–6] where the quality of a sample is characterised by the centre of the spectrum represented in polar co-ordinate system. Thus, the *x,y* co-ordinates of the centre (the quality point of a sample) can be determined from the formulae:

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$$x = \frac{1}{k}\sum_{i=0}^{k-1} V_{\lambda 1} \cos i\alpha \qquad y = \frac{1}{k}\sum_{i=0}^{k-1} V_{\lambda 1} \sin i\alpha \tag{1}$$

where V_{λ_i} is the spectral value measured at i_{th} wavelength, $\alpha = 360/k$, $k = (\lambda_{max} - \lambda_{min})/s$ and s is the wavelength difference between two adjacent spectral data points

The spectral region giving the best separation of the quality points of two groups can be optimised for the greatest sensitivity (S) defined by

$$S = \frac{D_{abs}}{s_1 + s_2} \qquad D_{norm} = \frac{D_{abs}}{D_{abs} + s_1 + s_2} \tag{2}$$

where s_1 and s_2 are the standard deviations of the quality points of the two repeatedly measured sample sets and Dabs is the absolute distance between the centres of the quality points of the two sample sets to be distinguished. Another optimisation criterion can be the normalised distance D_{norm} (Figure 1).

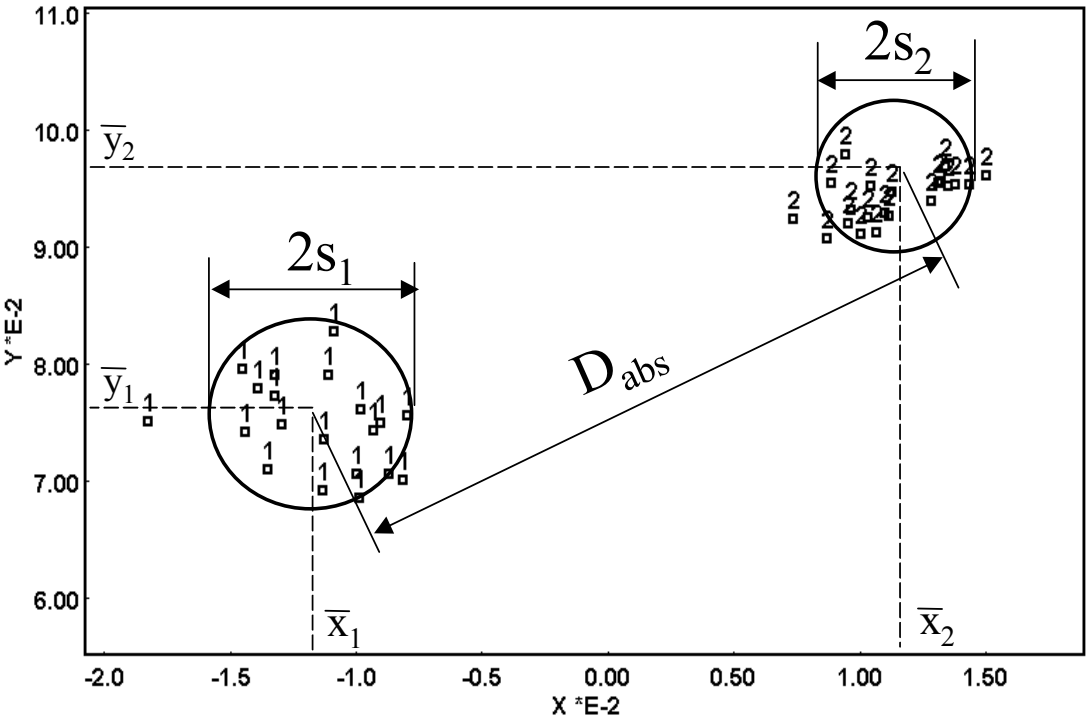

Figure 1. Graphical representation of the sensitivity and normalised distance as possible optimisation criteria.

By calculating these terms the effectiveness of the classification can be expressed numerically allowing comparison of different classification models. Within PQS a computer program performs wavelength range optimisation automatically. In this case parameters such as the first and last wavelength (within the optimal wavelength range which has to be searched for), the gap (the initial wavelength range), the gap shift and the gap broadening must be specified. Two groups of spectra consisting of repeated measurements of the two sample sets to be distinguished are required.

The "gap" is the length of the initial wavelength range in nm, which is then shifted with the "gap shift" in nm during the optimisation process from the first wavelength until the gap reaches the last wavelength. Then the gap broadens with the "gap broadening" in nm until the gap reaches the length of the whole wavelength region i.e. the difference between the first and last wavelength.

An important advantage of PQS compared with MLR is that PQS uses automatic range optimisation and so does not need an accurately analysed sample set, which is a requirement for MLR (where the calibration models are created to determine the relationship between the NIR spectra of the sample set and their quality parameters determined by reference methods). With PQS several optimal wavelength ranges can be used together giving better results while it is forbidden with MLR because of the collinearity problem.

Although in PQS the terms standard error of calibration and standard error of prediction are not interpreted, a similar term the uncertainty of the determination of the percentage of meat and bone meal in fish meal can be estimated from the value of the sensitivity. This shows the number of times that the absolute distance is greater than the sum of the standard deviations. This result may be improved by using more repeat measurements, or by taking into account other wavelength ranges, and by optimising the gap used to produce the second derivative, etc.

Results

For wavelength range optimisation, the spectra of the 46 pure fishmeal samples were treated as one group of repeated measurements while the spectra of each of the three groups of 30 contaminated samples were also treated similarly as groups of repeated measurements. Performing optimisation between pure fishmeal and the 9% contaminated samples, using the absolute value of the second derivative spectra (16 nm gap), identified the wavelength segment 1696-1752 nm as the optimum diagnostic region . This region was then re-scaled to span 0° to 360° in polar co-ordinate space (Figure 2). With the above conditions S=10,3, D_{norm}=9,1 were found.

To demonstrate classification by the PQS method, 5 spectra were randomly selected from each of the four groups and their spectra averaged. Thus five spectra were averaged to give 9 mean spectra representing the control (pure fishmeal) samples and 6 mean spectra from each of the three adulterated groups (3%, 6% and 9%). The four groups are shown surrounded by their 2s (two standard deviations) ellipse (Figure 3). The 2s ellipse for control samples (pure fish meal) is small, while the ellipse for the 9% contaminated samples is elongated probably as a consequence of inhomogeneity (imperfect mixing or sampling).

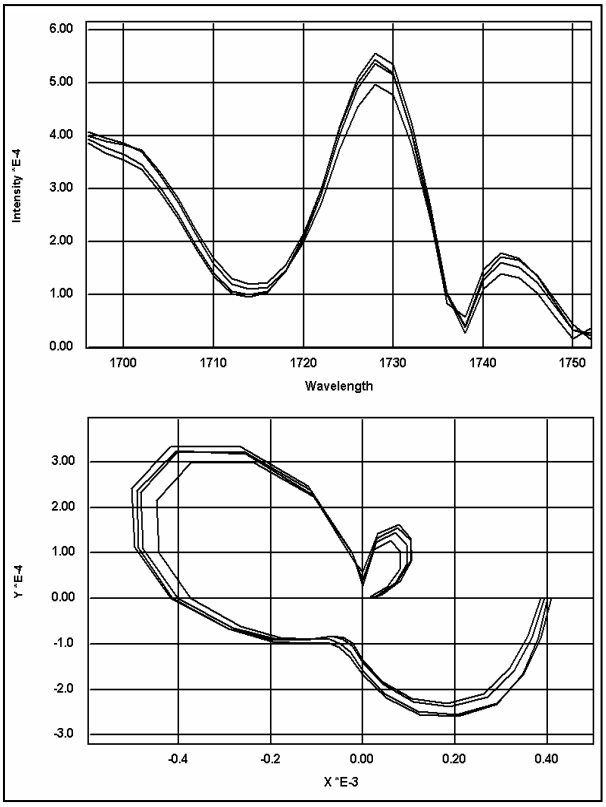

Figure 2. Second derivative spectra (16 nm gap) of pure and MBM-adulterated fishmeal samples in the optimal wavelength range 1696-1752 nm represented in the rectangular (upper) and in the polar (lower) co-ordinate system. (control 0% red, 3% blue, 6% orange, 9% green)

Conclusion

The obtained value of sensitivity (S = 10,3) shows that the absolute distance is ten times grater than the sum of the standard deviations of the quality points of the 0% and the 9% groups. This means that PQS can detect less than 1% contamination by averaging five spectra. As the sample set was a "closed" population collected mainly from UK sources, expansion of the population is required before the model can be applied globally.

The optimal wavelength region (1696–1752 nm) shows that the discrimination is related to the differences in the C–H features as fishmeal contains more polyunsaturated fatty acid than meat and bone meals.

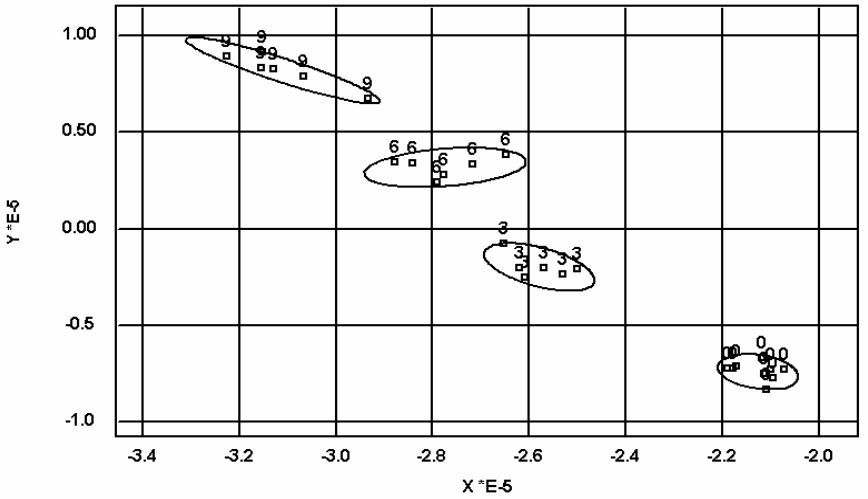

Figure 3. The quality points of the pure (0%, red) and MBM adultered (3% blue, 6% orange, 9% green) fishmeal samples using the optimal wavelength range only

References

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