Food Chemistry 210 (2016) 35–42

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

A feasibility study of non-targeted adulterant screening based on NIRM spectral library of soybean meal to guarantee quality: The example of non-protein nitrogen

Guanghui Shen [a], Xia Fan [b], Zengling Yang [a,*], Lujia Han [a]

[a] College of Engineering, China Agricultural University, Beijing 100083, PR China
[b] Institute of Quality Standard and Testing Technology for Agro-products of CAAS, Beijing 100081, PR China

ARTICLE INFO

Article history:
Received 24 November 2015
Received in revised form 14 April 2016
Accepted 20 April 2016
Available online 21 April 2016

Keywords:
Feed safety
Soybean meal
Near-infrared microscopy (NIRM)
Non-targeted detection
Non-protein nitrogen

ABSTRACT

The quality and safety of soybean meal is a key matter for the livestock breeding and food industries, since it is one of the most important and widely used protein feed raw materials. As driven by commercial interests, new illegal adulterants which are unknown to consumers and regulators emerge constantly. In order to make up for the inadequacy of traditional detection methods, a novel non-targeted adulterant screening method based on a near-infrared microscopy spectral library of soybean meal is proposed. This study focused on the feasibility of non-targeted screening methods for the detection of adulteration in soybean meal. Six types of non-protein nitrogen were taken as examples and partial least squares discriminant analysis was employed to verify the feasibility of this novel method. The results showed that the non-targeted screening method could screen out adulterations in soybean meal with satisfactory results.

1. Introduction

Soybean meal, a by-product of soybean oil extraction, with abundant protein, carbohydrate, dietary fibre, vitamins and minerals, is used as high-protein animal feed in many countries (Fernández Pierna et al., 2014). As driven by commercial interests, many types of illegal ingredients have been found in soybean meal with the purpose of increasing the nitrogen content (Bisaz & Kummer, 1983; Dorne et al., 2013). The standard protein determination method (i.e. Kjeldahl) cannot differentiate between protein nitrogen and non-protein nitrogen. Melamine (2,4,6-triamino-1,3,5-triazine), an adulterant used to increase the nitrogen content of foods and feeds, has caused illness and death of human infants and pets (cats and dogs), due to kidney damage (Administration, 2007; Organization, 2009; Reimschuessel & Puschner, 2010). In order to ensure food and protein feed safety, many platforms have been used to detect melamine, such as enzyme-linked immunosorbent assays (ELISA) (Yin et al., 2010), gas-chromatography mass-spectrometry (GC–MS) (Hong et al., 2009), high-performance liquid chromatography (HPLC) (Venkatasami & Sowa, 2010), near-infrared reflectance spectroscopy (NIRS) (Haughey, Graham, Cancouët, & Elliott, 2013), NIR hyperspectral imaging (Fu et al., 2014), NIR microscopy (NIRM) (Yang, Wang, Han, Li, & Liu, 2014) and so on.

The detection modes of all the methods mentioned above are targeted to detect the known and reported illegal compounds in food and feed. Although those methods for the detection of known adulterants are efficient, they cannot be used for screening an emerging illegal adulterant. There is an urgent need to investigate ways to avoid future melamine-type crises. Without knowing the emerging illegal adulterants we propose a non-targeted screening method, which could detect abnormal components of food or feed caused by adulteration. Taking the feed itself as the fidelity target would make feed safety control proactive, rather than being one step behind the adulterators (Lachenmeier et al., 2009).

Near-infrared spectroscopy (NIRS) is a convenient analytical method that has been applied in a wide range of studies involving quality control and adulteration detection (Haughey et al., 2013; Teye et al., 2015). NIRS has become an important tool of analysis due to its speed, non-destructiveness and reproducibility. NIRM which combines NIRS and digital images together to characterise samples in micro scale could provide more detailed information (Yang et al., 2014). NIRM spectral data are three-dimensional: $x \times y \times \lambda$, of which x and y are the spatial information and λ represents the spectral information. Each spectrum represents the sample information within each pixel (Gendrin, Roggo, & Collet, 2007; Huang, Tian, Min, Xiong, & Du, 2015; Kamruzzaman, ElMasry, Sun, & Allen, 2011). NIRM technology could collect hundreds or

* Corresponding author at: China Agricultural University, No. 17 Qinghua Donglu, Haidian District, Beijing 100083, PR China.
E-mail address: yangzengling@cau.edu.cn (Z. Yang).

http://dx.doi.org/10.1016/j.foodchem.2016.04.101
0308-8146/

thousands of spectra (including tens or hundreds of variables) for each sample, instead of unique average spectra. NIRM technology almost does not damage or consume sample in the process of analysis and requires minimal sample preparation (Huang, Min, Duan, Wu, & Li, 2014; Pierna et al., 2012). Based on these advantages, NIRM is now applied as an advanced analytical method in many fields such as pharmaceutics (Amigo et al., 2008; Cruz, Bautista, Amigo, & Blanco, 2009; Gendrin, Roggo, & Collet, 2008), meat quality evaluation (He & Sun, 2015), and food and feed safety control (Jiang, Yang, & Han, 2014; Pierna et al., 2012).

In this paper we developed a non-targeted screening method for the detection of adulterations in soybean meal. Six types of non-protein nitrogen compound (melamine, cyanuric acid, urea, biuret, mono-ammonium phosphate (MAP) and di-ammonium phosphate (DAP)) were selected as adulterants. Global H (GH) value discrimination method based on the spectral library of soybean meal was employed to select spectra of non-protein nitrogen sources in the mixtures. Partial least squares discriminant analysis (PLSDA), which is a supervised classification method successfully used for discriminant analysis in many fields (Cozzolino, Chree, Scaife, & Murray, 2005; de Almeida, Correa, Rocha, Scafi, & Poppi, 2013; Pierna et al., 2014), was used to verify the feasibility of the non-targeted screening method based on GH value.

2. Materials and methods

2.1. Experimental strategy

A novel non-targeted adulterant screening method based on an NIRM spectral library of soybean meal was proposed for abnormal spectra selection in artificially mixed samples. For verifying the feasibility of the novel method the PLSDA, which has been successfully used for the detection of melamine and cyanuric acid in feed, was employed (Fernandez Pierna et al., 2014). The flowchart of the experimental strategy for this study is shown in Fig. 1.

2.2. Sample collection and preparation

Soybean meal samples ($n = 88$), which were collected from Argentina, Italy, Brazil, France and China, were used in this study and ground to pass through a 0.5-mm square mesh using a Retsch mill (Ultra centrifugal Mill ZM 100; Retsch GmbH, Haan, Germany). Melamine, cyanuric acid, urea, and di-ammonium phosphate (DAP) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Biuret was bought from Tianjin Fuchen chemical reagents factory (Tianjin, China). Mono-ammonium phosphate (MAP) was purchased from Beijing chemical reagent company (Beijing, China).

Exploratory principal components analysis was applied to the 88 average spectra of soybean meal samples. Different types of soybean meal samples were separated into different groups. One sample from each group was selected randomly and prepared for adulteration analysis in this study. A complete strategy and sampling is detailed in Section 3.1 of this paper.

Set 1 and set 2 were prepared for adulteration analysis in this paper as shown in Table A 1. All the mixtures were prepared in the laboratory using a mixer (REAX 20/8; Heidolph, Schwabach, Germany). In order to reach a homogeneous distribution of adulterants in the soybean meal, a stepwise dilution procedure was applied to ensure that in each dilution step the ratio of the two materials to be mixed did not exceed a factor of 3 (Gizzi, von

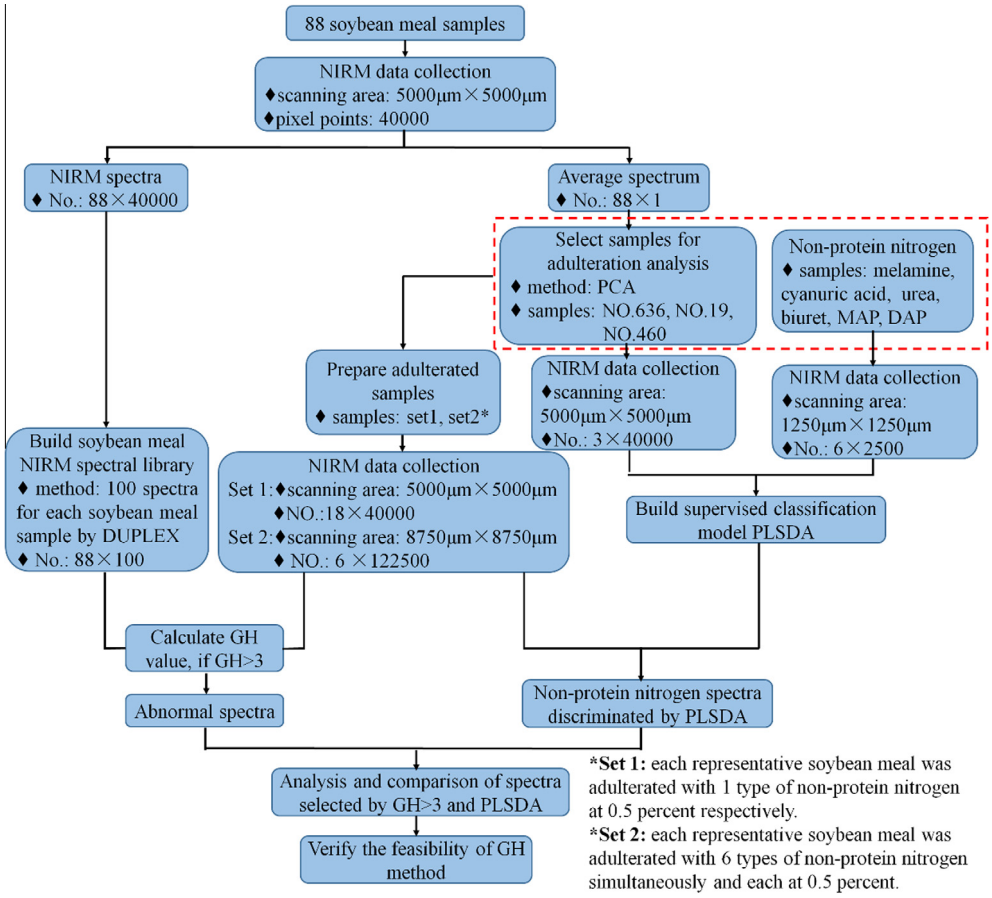

Fig. 1. Experimental flowchart for this study.