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The feasibility of using near infrared and Raman spectroscopic techniques to detect fraudulent adulteration of chili powders with Sudan dye

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ABSTRACT

Chili powder is a globally traded commodity which has been found to be adulterated with Sudan dyes from 2003 onwards. In this study, chili powders were adulterated with varying quantities of Sudan I dye (0.1–5%) and spectra were generated using near infrared reflectance spectroscopy (NIRS) and Raman spectroscopy (on a spectrometer with a sample compartment modified as part of the study). Chemometrics were applied to the spectral data to produce quantitative and qualitative calibration models and prediction statistics. For the quantitative models coefficients of determination (R^2) were found to be 0.891–0.994 depending on which spectral data (NIRS/Raman) was processed, the mathematical algorithm used and the data pre-processing applied. The corresponding values for the root mean square error of calibration (RMSEC) and root mean square error of prediction (RMSEP) were found to be 0.208–0.851% and 0.141–0.831% respectively, once again depending on the spectral data and the chemometric treatment applied to the data. Indications are that the NIR spectroscopy based models are superior to the models produced from Raman spectral data based on a comparison of the values of the chemometric parameters. The limit of detection (LOD) based on analysis of 20 blank chili powders against each calibration model gave 0.25% and 0.88% for the NIR and Raman data, respectively. In addition, adopting a qualitative approach with the spectral data and applying PCA or PLS-DA, it was possible to discriminate between adulterated chili powders from non-adulterated chili powders.

1. Introduction

In the modern era, there is a growing concern with regards to food fraud. This has been highlighted by the recent European wide horse meat and pig meat in beef scandal which has raised awareness with the media and the general public that food fraud is a practice that is widespread and remains largely undetected. Although this scandal was a food chain integrity issue, there are instances of food fraud which are safety issues where consumers can become ill or die. These include the melamine adulteration of milk powder scandal in China which affected ~300,000 children with six reported deaths (Andersen et al., 2008; Brown et al., 2007; Ehling, Tefera, & Ho, 2007; Gossner et al., 2009; Yan, Zhou, Zhu, & Chen, 2009), and in the Czech Republic where vodka adulterated with methanol resulted in at least 38 deaths due to chemical poisoning (European Union Rapid Alerts System for Food and Feed (EU RASFF) Annual Report 2012). According to Spink and Moyer (2011), food fraud is a collective term used to encompass the deliberate and intentional substitution, addition, tampering, or misrepresentation of food, food ingredients, or food packaging; or false or misleading statements made about a product, for economic gain.

Herbs and spices are globally traded commodities that are used in many industries and as such have been found to be fraudulently manipulated. This was highlighted from 2003 onwards where the intentional addition of Sudan dyes to spices, used to intensify and maintain their natural appearance (EUROPEAN COMMISSION DECISION 2003/460/EC). Sudan dyes are classified as Class 3 carcinogens (IARC, 1975 , pp. 224–231) and are therefore banned worldwide as a food additive for

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human consumption. The first notifications from the European Union Rapid Alerts System for Food and Feed (EU RASFFs) related to this type of fraud were raised due to adulteration of chili products from India being identified (Oplatowska, Stevenson, Schulz, Hartig, & Elliott, 2011). By 2005, the EU had put in place regulatory legislation (EUROPEAN COMMISSION DECISION, 2005/402/EC) which required member states to monitor imported foodstuffs for the presence/absence of Sudan dyes which was subsequently repealed and replaced in 2009 with a regulation which contained a less onerous testing regime due to a decrease in positive results (EUROPEAN COMMISSION REGULATION (EC) No 669/2009).

Many analytical methods have been developed for the determination of the adulteration of spices. Recently the use of fingerprinting techniques as rapid methods for the detection of food adulteration and contamination have been reviewed in an excellent overview of this area (Ellis et al., 2012). The use of existing or new technologies, to produce 'fingerprints' for human foods, animal feeds and animal health, is gaining interest for many applications due to being rapid robust techniques. Vibrational spectroscopy techniques are amongst the emerging molecular fingerprinting methods that are becoming more widely used in feed and food screening analysis (Ellis et al., 2012). Near infrared spectroscopy (NIRS), based on the absorption of certain wavelengths of light (800 nm–2500 nm, 12,500 cm^{-1}–4000 cm^{-1}), and Raman spectroscopy, based on the inelastic scattering of light, are becoming increasingly popular tools in the determination of food adulteration. In the tracing and verification of the origins of foods and determining the authenticity of food products, a range of spectroscopic techniques have been shown to deliver data that can provide evidence based on the molecular structure/composition of the samples being tested. With regards to the detection of chemical adulterants in foods, Raman spectroscopy has recently been shown to be capable of detecting melamine in milk (Zhang et al., 2010). In addition, NIRS methods of detecting the adulteration of melamine in soya bean products (Haughey, Graham, Cancouet, & Elliott, 2013) and NIRS and Raman to detect waste oil adulteration in animal feed oils (Graham et al., 2012) have been successfully developed and validated. The potential of Raman spectroscopy for the determination of melamine adulteration of animal feed and foodstuffs has also been assessed (Liu et al., 2009). NIRS has been used previously to determine contamination/adulteration of spice commodities which included mycotoxins such as aflatoxin B1 in red paprika (Hernandez-Hierro, Garcia-Villanova, & Gonzalez-Martin, 2008) and red chili powder (Tripathi & Mishra, 2009). The same technique has been applied to saffron spice to determine its chemical composition and geographical origin and validated by comparison with UV–Vis and HPLC_DAD measurements (Zalacain et al., 2005). Another technique that has been successfully used to determine adulteration of spices with Sudan I–II–III–IV dyes was UV–Vis spectroscopy (Di Anibal, Oden, Ruisáncheza, & Callaoa, 2009). Surface enhanced Raman scattering (SERS) has been employed to detect Sudan I dye at low contamination levels (10^{-3}–10^{-4} mol L^{-1}) in spices including chili powders using both extraction and non-extraction techniques and highly specialised specific colloidal substrates for enhancement of the signals (Cheung, Shadi, Xu, & Goodacre, 2010; Di Anibal, Marsal, Callao, & Ruisánchez, 2012).

The aim of the present feasibility study was to evaluate the potential of NIR and Raman spectroscopies, with a modification to the latter instrument, as screening tools for detecting adulteration of chili powders with the banned Sudan I dye. The spectral data was processed using chemometric software to develop calibration models with potential to detect this type of fraud.

2. Material and methods

2.1. Sample collection and preparation

Commercial samples of spices were purchased at various convenience shops, supermarkets and market places in the UK and Ireland in addition to a small number that were obtained from other non EU countries. A number of chili powders were selected and these were spiked with Sudan I dye (Fisher Scientific, Loughborough, England) at various concentrations (5%, 2.5%, 1%, 0.5%, 0.2%, 0.1% and 0% w/w, total samples $n = 112$). In addition 20 blank chili powders were used to determine the limit of detection (LOD) of each calibration model produced from the NIR and Raman spectra data.

2.2. Near-infrared spectroscopy

Near-infrared spectra, obtained using reflectance mode, were recorded on an Antaris II FT-NIR (Thermo Fisher Scientific, Dublin, Ireland). The samples of spices (10 g) were poured onto the sample cup (5 cm) spinner on the Integrating Sphere module of the instrument. All the spectra were computed at 8 cm^{-1} resolution across the spectral range 12,000–4000 cm^{-1} and ran in triplicate with the sample cup being refilled on each occasion. Instrument control and initial spectral manipulation were performed with Result Integration software. The spectra were recorded at ambient temperature and a total of 64 scans were acquired for each spectrum.

2.3. Modification of the Raman spectrometer sample compartment

2.3.1. Components needed for modification

The following items were purchased to build a new sample compartment: Metric bench plate (600 mm × 300 mm), Double-convex (DCX) lens (25 mm diameter with 25 mm effective focal length), Lens Holder, Post Holders, Stainless Steel Mounting Posts (Edmund Optics Ltd, York, UK), Dexion Speed Frame (25 mm tube × 3048 mm) including joints (type 4.1) and inserts (Stodec Products Ltd, St. Albans, UK), Palight Foam PVC (2.44 m × 1.22 m × 3 mm) (Magco, Dublin, Ireland), Spinner-MFA – 918D1001 motor/gearbox with shroud (CPC, Preston, UK).

2.3.2. Prototype sample compartment and sample spinner for Raman instrument

The Delta Nu Advantage 1064 Raman spectrometer is supplied with a simple fixed sample compartment which accepts glass vials that can be filled with liquid or solid samples as required. This fully enclosed system allows the laser to be focussed onto a point on the surface to optimise signal intensity but has no facility for recording a spectrum at more than a single point. This is acceptable for homogenous samples such as oils or other liquids and homogeneous powder samples but it can cause large sub-sampling errors with heterogeneous samples since the small sampling area (<<1 mm in diameter) means that spectra can be obtained from non-representative parts of the sample. To overcome this, a new sample compartment with the facility to rotate the sample during signal accumulation was constructed. The existing sample holder was removed to allow the laser beam to travel outside the spectrometer although the laser interlock system left intact since the system uses a 1064 nm laser which is invisible to the naked eye but is a high power Class 4 system. The laser was focused by an external a 25 focal length mm double-convex lens (DCX), (25 mm diameter) into the sample. This lens was chosen to maintain the high collection efficiency which in the unmodified system is obtained by using a very short focal length collections lens. It also has the