



# Non-targeted detection of paprika adulteration using mid-infrared spectroscopy and one-class classification – Is it data preprocessing that makes the performance?



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## ABSTRACT

A method for the non-targeted detection of paprika adulteration was developed using Fourier transform mid-infrared (FT-MIR) spectroscopy and one-class soft independent modelling of class analogy (OCSIMCA). One-class models based on commercially available paprika powders were developed and optimised to provide > 80% sensitivity by external validation. The performances of the established models for adulteration detection were tested by predicting spiked paprika samples with various types of fraudulent material and levels of adulterations including 1% (w/w) Sudan I, 1% (w/w) Sudan IV, 3% (w/w) lead chromate, 3% (w/w) lead oxide, 5% (w/w) silicon dioxide, 10% (w/w) polyvinyl chloride, and 10% (w/w) gum arabic. Further, the influence of data preprocessing on the model performance was investigated. Relationship between classification results and data preprocessing was identified and specificity > 80% was achieved for all adulterants by applying different preprocessing methods including standard normal variate (SNV), first and second derivatives, smoothing, and combinations thereof.

## 1. Introduction

Since ancient times spices have been used to flavour foods and improve the taste of dishes. Just as long dishonest practices have been going on in the food chain and the motivation for spice fraud is still the same since trading began – that is financial gain (Spink & Moyer, 2011). Because they are high value commodities and consumption is increasing worldwide, spice adulteration promise high economic profit. Taking this motivation together with the length and complexity of the supply chains make spices an attractive product category for fraudsters. The substitution of ingredients, addition of (illegal) substances, and false claims of origin are important and challenging issues food authorities and industry are confronted with (Esslinger, Riedl, & Faulh-Hassek, 2014). Colour is one of the main quality attributes of spices (van Asselt, Banach, & van der Fels-Klerx, 2018) and therefore, a common adulteration was found to be the addition of illegal dyes to artificially enhance and maintain the natural colour or to cover up blending with lower value product material (Silvis, van Ruth, van der Fels-Klerx, & Luning, 2017). In addition, the price of spices is often determined by their weight or volume, and therefore another common spice adulteration is the addition of less expensive bulking agents (Petrakis & Polissiou, 2017).

Paprika powder is one of the most frequently consumed spices in the European Union (van Asselt et al., 2018). It is obtained by grinding varieties of dried fruits belonging to the genus *Capsicum*. Numerous varieties of paprika having different colours, shapes, flavour, degree of hotness etc., are cultivated (Seliem, Mahmoud, Amin, & Salama, 2015). In the food industry paprika powder is used both as a natural colourant to adjust or intensify the colour of foodstuffs and impart flavour. Capsanthin, capsorubin, and other carotenoids are the pigments responsible for the characteristic colours whereas capsaicinoids are the pungency giving compounds which are produced in paprika at various levels depending on the variety (Palacios-Morillo, Jurado, Alcázar, & Pablos, 2016). Although spices like paprika powder are used and consumed only at low amounts, they are present in almost every processed food, and therefore authenticity testing of spices in general and paprika powder in particular has become an important topic in terms of consumer (health) protection.

Over time paprika powder was found to be fraudulently manipulated by addition of different materials that are for example not permitted as food additives in the European Union such as lead oxide (Döka, Bicanic, & Szöllösy, 1998) and synthetic dyes (van Asselt et al., 2018). Microscopic examination of paprika powder is the classical way for the detection of foreign material. While a powerful method it

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requires tremendous training and continuous practices. Many analytical methods have been suggested in recent years for the determination of azo dyes, especially carcinogenic Sudan dyes (Lohumi et al., 2017). The most common methods are based on high-performance liquid chromatography (HPLC) with ultraviolet–visible (UV–vis) absorbance or mass spectrometry (MS) detectors (Reinholds, Bartkevics, Silvis, van Ruth, & Esslinger, 2015). Although these methods are very sensitive with regard to the analysis of a specific compound or class of compounds, they are time-consuming and expensive. Hence, a lot of effort has been put into the development of rapid screening methods based on spectroscopic techniques for the detection of adulteration. Nuclear magnetic resonance (NMR) (Di Anibal, Ruisánchez, & Callao, 2011), fluorescence (Di Anibal, Rodríguez, & Albertengo, 2015), and UV–vis spectroscopy (Di Anibal, Rodríguez, & Albertengo, 2014), combined with multivariate classification techniques have recently been shown to be capable of detecting Sudan dyes in paprika in the sub-parts per million levels. Vibrational spectroscopic techniques including Fourier transform mid-infrared (FT-MIR) (Lohumi et al., 2017), near infrared (NIR), and Raman spectroscopy (Haughey, Galvin-King, Ho, Bell, & Elliott, 2015) have also been successfully applied to determine spice adulteration with Sudan dyes, although these methods are less sensitive.

In particular FT-MIR spectroscopy has become widely used as analytical screening tool for the authentication of feed and food due to its benefits such as the analysis of samples with minimal or even without any preparation, simple instrumentation, and rapid data collection. Its potential for adulteration detection of food is confirmed by the high number of studies in literature, e.g., on fruit juices, edible oils, honey, herbs, and numerous other food products (Black, Haughey, Chevallier, Galvin-King, & Elliott, 2016; Lohumi, Lee, Lee, & Cho, 2015; Rodriguez-Saona & Allendorf, 2011). In most studies, multivariate regression or discriminant models were applied to FT-MIR spectral data which allowed for the detection of selected adulterants. However, this targeted strategy would fail in screening samples where other types or yet unknown adulterants are present. Indeed, this is the big challenge in the detection of adulteration using targeted analytical approaches that only substances that are being investigated are usually found, whereas unknown or unforeseen adulterants might be overlooked. Therefore, non-targeted approaches have increasingly become a focus of research.

Combining spectroscopic methods with chemometric one-class modelling techniques creates a powerful tool to enable detections for a range of both known and unknown adulterants. One-class classifiers are commonly applied when the data from other classes is hard to collect (Oliveri, 2017), for example in food authentication it is nearly impossible to make an exhaustive analysis and take all potential adulterants into account. Although considered to be very suitable, in food sciences there are only few examples using the one-class classification approach for non-targeted adulteration detection including the detection of several adulterants in rice flour (Xu, Yan, Cai, & Yu, 2013), kudzu starch (Xu, Shi, Cai, Zhong, & Tu, 2015), and skim milk powder (Capuano, Boerrigter-Eenling, Koot, & van Ruth, 2015) by NIR spectroscopy, as well as in raw milk (Gondim, Junqueira, de Souza, Ruisánchez, & Callao, 2017), and sesame oil (Xu et al., 2012) by FT-MIR spectroscopy. Here, one-class modelling techniques were used to objectively classify samples into “normal” (authentic) and “abnormal” (adulterated) samples. For designing such one-class model a representative set of samples is required covering the most important sources of variation within the class of interest (Xu, Shi et al., 2015). For non-targeted adulteration detection, the class of interest is the “normal” class consisting of authentic samples. They serve as the basis for determining the data space of the authentic product and detecting whether a new sample is similar to the defined “normal” (authentic) class (Kjeldahl & Bro, 2010). This is the main difference to multi-class classification where also the “abnormal” classes are required to classify new samples.

The usefulness of a developed one-class model should be sufficiently

validated with new samples, both authentic and adulterated samples. The classification performance depends on many aspects such as size and representativeness of the baseline sample set as well as the number and quality of the (preprocessed) spectral data. Proper preprocessing is required to remove unwanted variations and highlight differences caused by adulteration (Xu, Shi et al., 2015; Xu et al., 2013) and therefore testing several preprocessing methods is an essential part of the chemometric workflow. Nevertheless, preprocessing optimised in a study for a certain type of adulterant carries the risk that other adulterants will be overlooked.

The aim of the current study was to develop and validate a simple screening method for the non-targeted detection of adulteration of paprika powder. For this, FT-MIR spectroscopy coupled with one-class soft independent modelling of class analogy (OCSIMCA) was tested. Combining a spectroscopic technique with multivariate one-class classification method seemed to be the most promising strategy to determine any deviations from typical paprika powder characteristics and therefore to detect various adulterants within one approach. Moreover, as integral part of chemometrics different data preprocessing methods were applied in order to examine a potential influence on the model performance results.

## 2. Material and methods

### 2.1. Sample collection and preparation

A total of 113 samples of paprika powder were investigated in this study. Fifty of these samples (all from different batches) were provided with metadata about provenance, harvest year, extractable colour, and pungency by one company in course of the EU project SPICED (Székács, Wilkinson, Mader, & Appel, 2018). Further 63 commercially available samples of 32 different brands (1–6 batches per brand) were purchased from various retailers in Germany including supermarkets and market places. Thus, the paprika powder sample set covers the major relevant sources of natural variation such as quality (e.g., colour and pungency), provenance, harvest year, production, and storage condition/packaging. All samples were stored at room temperature in the dark under clean and dry conditions.

A principal component analysis (PCA) of the FT-MIR data of the 113 paprika powders was performed to identify a representative subset for artificial adulteration. From the PCA scores plot of the first two principal components (PCs) ten paprika powder samples (9 brands) were selected that cover the main variation of the paprika data set. These samples were spiked with 7 potential colouring or bulking adulterants, namely gum arabic, lead chromate, lead (II, IV) oxide, polyvinyl chloride (PVC), silicon dioxide, Sudan I, and Sudan IV, respectively. The selection of adulterants is based on notifications in the European Rapid Alert System for Food and Feed (RASFF) and reports in the Food Fraud Database of the U.S. Pharmacopeial Convention (USP) and derived from expert opinions. The aim was to cover various types of well-known and potential adulterant materials including organic as well as inorganic substances. The selected adulterants have not necessarily been reported or observed in paprika powder in the past. Concentrations were chosen according to the adulteration purpose, with lower levels for dyes that still have an effect on the colour of paprika powder and higher, economically relevant adulteration levels for bulking agents. Adulterants were added at levels of 1.0 (Sudan I, Sudan IV), 3.0 (lead chromate, lead oxide), 5.0 (silicon dioxide), and 10.0 (gum arabic, PVC) g/100 g (w/w) under gravimetric control (Sartorius ME254S analytical balance). The entire number of artificially adulterated samples was 70.

Prior to FT-MIR analysis the samples, both non-adulterated and artificially adulterated paprika samples, were ground to a homogeneous powder. For this, approximately 0.8 g solid material were weighed into grinding jars (Retsch 10 mL zirconium oxide jar and 2 zirconium oxide grinding balls with 12 mm diameter) and milled at 30 Hz for 2 min

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