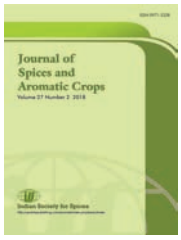
Journal of Spices and Aromatic Crops
Vol. 27 (2) : 106–118 (2018)
doi : 10.25081/josac.2018.v27.i2.1099

Indian Society for Spices



Instrument-based detection methods for adulteration in spice and spice products – A review

S K V Bharathi, A Sukitha, J A Moses* & C Anandharamakrishnan

Indian Institute of Food Processing Technology
Ministry of Food Processing Industries, Govt. of India,
Thanjavur-613 005, Tamil Nadu.
**E-mail: moses.ja@iifpt.edu.in*

Received 15 May 2018; Revised 16 July 2018; Accepted 25 October 2018

Abstract

Spices play an important role as flavorants, colorants, preservatives and bioactive compounds in medical, food and cosmetic applications. India is the spice bowl of the world and spice production is scattered across the country. Almost every stage of production, including cultivation, harvest, handling, storage, transportation and distribution has impact on spice quality. Adulterants are often intentionally added to fetch better market value through inferior/ unacceptable quality products. Adulterants are a concern to quality, market compliancy and food safety. Over the years, several approaches for quantitative and qualitative detection of adulterants have been developed. Though basic and simple testing methods are available to detect the presence of adulterants, instrument-based techniques are often adapted to detect the adulterants quantitatively. The objective of this work is to present a detailed note on these approaches with emphasis on the various analytical techniques used in the detection and quantification of adulterants in spice and spice products.

Keywords: adulteration, adulterants, detection, quality, quantitative, qualitative, spice

Introduction

India being the spice bowl of the world produces over 7 million tonnes of different spices every year. Among the 109 types of spices enlisted by International Organization for Standardization, India produces more than 65 varieties. In India, about 3.15 million hectares of land is under spice cultivation. During 2015-2016, the country exported spice worth 2482.83 million US$ by exporting 0.84 million tonnes of spices and such huge figures indicate the massiveness of Indian spice products in the global export market (Spices Board 2017).

Spices are mainly valued for their characteristic flavor, aroma and color (Moses *et al.* 2014). Since ancient times, spices have been products of high economic value and possess broad range of applications in various fields; including, culinary,

medicinal and cosmetic usage (Peter & Zachariah 2000). They are classified as: major spices, tree spices, seed spices and other spices (Bharath *et al.* 2017). Post-harvest losses in spices is heavy (Alice *et al.* 2016) and the risk of contamination and adulteration in spices is a growing concern. Very often they cause severe health hazards in humans apart from obvious loss in product quality.

Adulteration is the intentional or unintentional inclusion of substances that are not legally approved in foods, leading to an imitation of the product and ultimate reduction in market value (Manning & Soon 2014). Intentional or economic adulteration is done to mimic enhanced visual and organoleptic quality by the addition of foreign materials. Foreign matter such as floral wastes, fraudulent components including artificial colorants, spent extracts and plant parts of foreign species are the commonly detected adulterants. Selected examples are presented in Table 1. Indirect or unintentional adulteration involves inclusion of substances in food due to ignorance or the lack of knowledge. This can occur due to inappropriate processing and handling operations. For example, harvesting in the wrong period, improper drying, poor storage conditions and gross substitution with plant materials like presence of stalk with pepper berries are practical concerns (Silvis *et al.* 2017).

In order to ensure food safety and food quality, various methods are used to detect and quantify adulteration in spices. In general, basic testing methods are used for qualitative detection, whereas instrumental techniques are used for quantitative detection of adulteration in spices. Several instrumental techniques (often used in conjunction with chemometric techniques) have been used and with advancements in analytical chemistry, most modern methods are known for their sensitivity, accuracy, selectivity and rapidity. Recently, molecular techniques are also being explored for detection of adulterants in spice and spice products (Table 2).

Instrumental methods for quality evaluation of spices

Approaches for qualitative evaluation using instruments can be classified on the basis of the chemical or physical property that is the essential differentiating factor. Chemical reactivity, polarity, solubility, molecular weight, melting point, boiling point, absorptivity, emissivity and mass spectra are examples (Skoog *et al.* 2017). Instrumental analysis can be performed individually or in combination to provide a synergistic approach for both adulterant detection and authentication. According to International Union of Pure and Applied Chemistry, "In quantitative analysis the amount or concentration of an analyte may be determined (estimated) and expressed as a numerical value in appropriate units and it requires the identification (qualification) of the analyte for which numerical estimates are given" (McNaught & Wilkinson 1997). Chemometrics, the multi-dimensional analysis approach, is usually integrated with analytical instrumentations. This facilitates identification of the functional group of unidentified adulterants by comparing their morphology, chemical and biochemical characteristics with a known sample (Otto 2016). Comparison tests can be done on the basis of learning algorithms

Table 1. Selected list of common adulterants in spices (Toteja *et al.* 1990)

Spice	Adulterant
Black pepper (*Piper nigrum*)	Dried papaya seeds, light berries
Red chilli (*Capsicum annuum*) powder	Brick powder
Mustard seeds (*Brassica nigra*)	Argemone seeds
Turmeric (*Curcuma longa*)	Metanil yellow
	Lead chromate
Ground spices	Sawdust, bran
Coriander (*Coriandrum sativum*) powder	Common salt

Table 2. Examples of molecular approaches for quality evaluation of spices

Approach	Spice/ Spice product(s)	Adulterant detected	Limit of detection	References
Random Amplified Polymorphic DNA	Red chilli (*Capsicum annuum*) powder	Plant based adulterants like dried red beet pulp, almond shell dust and powdered Jharber (*Ziziphus nummularia*) fruits.	5%	(Dhanya *et al.* 2008)
Sequence Characterized Amplified Region (SCAR) markers	Saffron (*Crocus sativus* L.)	Flowers of Mountain arnica (*Arnica montana* L.), Achiote (*Bixa orellana* L.), English marigold (*Calendula officinalis* L), safflower (*Carthamus tinctorius* L.), spring crocus (*Crocus vernus* L. (Hill)), day lily (*Hemerocallis* sp.) and rhizomes of turmeric (*Curcuma longa* L.)	1%	(Marieschi *et al.* 2012)
	Turmeric (*Curcuma longa* L.) powder	Other *Curcuma* species like *C. zedoaria* and *C. malabarica*	1%	(Dhanya *et al.* 2011b)
	Ground chilli (*Capsicum annuum*)	Dried red beet pulp and powdered Jharber (*Ziziphus nummularia*) fruits	1%	(Dhanya *et al.* 2011a)
	Black pepper (*Piper nigrum* L.) powder	Papaya seed (*Carica papaya* L.) powder	1%	(Dhanya *et al.* 2009)
SCAR and Internal Transcribed Spacer (ITS) reliable multiplex Polymerase Chain Reaction (PCR)-based assay	Saffron (*Crocus sativus* L.)	Safflower (*C. palestinus, C. oxyacanthus* and *C. tinctorius*)	-	(Baker *et al.* 2014)
DNA barcoding	Saffron *Crocus sativus* (L.)	Safflower (*Carthamus tinctorius* L.), English marigold (*Calendula officinalis* L.) flowers, day lily (*Hemerocallis* L.) petals, carrot (*Daucus carota* L.) fleshy root, turmeric (*Curcuma longa* L.) rhizomes, maize *(Zea may* L.) and lotus (*Nelumbo nucifera* Gaertn.) stigmas	-	(Jiang *et al.* 2014)
	Turmeric (*Curcuma longa* L.) powder	Wild species of *Curcuma* like *C. zedoaria* and cassava starch	-	(Parvathy *et al.* 2015)
	Cinnamon (*Cinnamomum verum*)	Inferior species like *C. cassia* and *C. malabatrum*	-	(Swetha *et al.* 2014)
	Black pepper (*Piper nigrum* L.) powder	Chilli (*Capsicum annuum*) powder	0.5%	(Parvathy *et al.* 2014)
Single Strand Conformation Polymorphism (SSCP) Sequencing	Differentiation of *Cinnamomum* species like *C. cassia, C. zeylanicum, C. burmannii* and *C. sieboldii*		-	(Kojoma *et al.* 2002)

(principle component analysis (PCA), soft independent modelling by class analogy (SIMCA), partial least squares (PLS), artificial neural network (ANN) and k-nearest neighbour (kNN) by referring a developed database.

Spectroscopic methods of analysis

In general, the spectroscopic methods involve creating, measuring and interpreting the interaction of electromagnetic radiation with the substance (Penner 2017). Spectroscopic methods can be broadly divided based on the species to be analyzed, type of radiation and also based on the type of radiation-matter interaction, as illustrated in Fig. 1 (Penner 2017).

Spectroscopy is possible when the photon's interaction with a sample leads to a change in energy, velocity, amplitude, frequency, phase angle, polarization or direction of propagation (Kerker 2016). In absorption spectroscopy, energy of the photons is absorbed by the sample, leading to excitation of valence electrons to higher energy levels or changes in vibrational/ rotational energies of chemical bonds, depending on the wavelength or frequency of the spectral region. Since energy levels are quantized, absorption occurs only if the energy of a photon matches the energy difference between two energy levels. In emission spectroscopy, electrons from higher energy levels return to lower energy levels following emission of photons (Harvey 2000).

A typical spectroscopic instrument consists of an energy source to generate the electromagnetic spectrum, a wavelength selector such as a monochromator to narrow the range of wavelengths to be used, a sample holder, a sensitive detector such as a photon or thermal transducer for measuring signals and a signal processor for manipulating captured signals to a readable form (Vermaak *et al.* 2014). This section gives an overview of the common spectroscopic techniques that have been used in the detection of adulterants in spice and spice products.

UV-Vis spectroscopy

Principle

UV-Vis spectroscopy is based on the principle of Beer-Lambert's law. It states the relationship between the amount of radiation absorbed by the solution and the concentration of the solution (Swinenhart 1962).

$A = \log_{10} (I_0/I) = áLC$

Where, I_0 and I are the Intensities of the light; á refers to molar absorptivity; L is the length of the beam in the absorbing medium; C is concentration of the absorbing species.

Method

Typically, analytical measurements in UV-Vis spectroscopy are carried out between 200 to 800 nm (Isengard & Breithaupt 2015). The radiation source for UV-Vis spectroscopy could be a hollow cathode lamp, a tungsten filament lamp or a mercury vapour lamp. The sample can either be a liquid or a solid dissolved in suitable solvents. The sample is placed in a cuvette and enclosed in a compartment which prevents the loss of radiation and the possibility of interference from

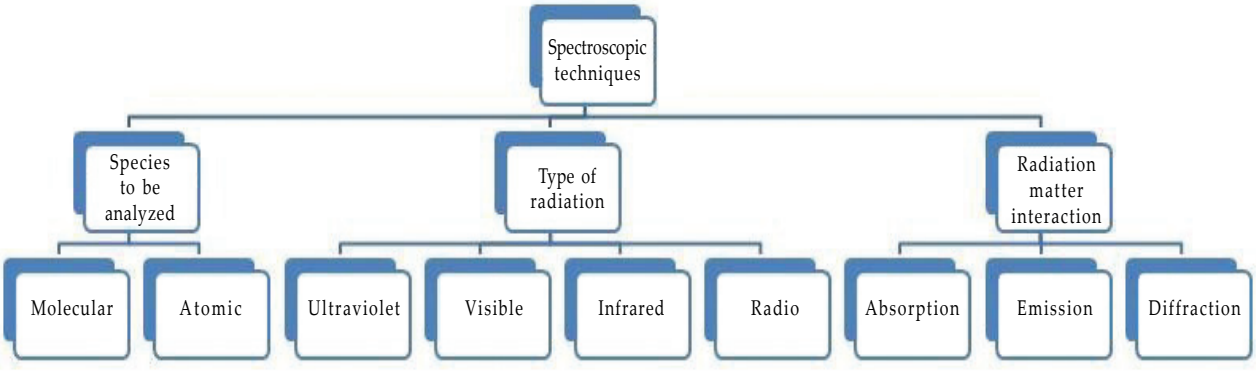


Fig. 1. Spectroscopic methods used for analysis

any stray radiations. Electromagnetic radiation from the source hits a filter/ monochromator, producing a spectrum of particular wavelength. The obtained spectrum is allowed to pass through a shutter. Monochromatic light hits the sample and energy is absorbed by the molecules present in it. A sensitive photon transducer converts this absorbed energy into electrical signals and a signal processor displays it digitally (Kealey & Haines 2002).

Di Anibal *et al*. (2014) successfully demonstrated UV-Vis spectroscopy as an alternative to classical methods by detecting adulteration in culinary spices (upto 1-5 ppm) with Sudan I or blends of Sudan I and IV dyes and classified the samples as unadulterated or adulterated ones using a multivariate analysis screening tool. Addition of Sudan dye results in an increase in absorbance values and this increase is attributed to difference in chemical structure of the Sudan dyes (Di Anibal *et al*. 2009). UV-Vis spectroscopy has been a simple, fast and cost-effective tool for determining Sudan dye adulteration in spices.

Surface Enhanced Raman Spectroscopy

Principle

Surface enhanced Raman spectroscopy (SERS) works on a surface phenomenon that enhances the Raman scattering intensity by molecules in the vicinity of nano-structured metal surfaces (such as Au, Ag and Cu) when excited by electromagnetic radiation (Novák *et al*. 2016). The enhancement of Raman scattering is due to surface plasmon resonance, photon driven electron transfer, surface chemistry of nanoparticles being employed, and interaction between radiation and the material (Ding *et al*. 2014). The enhancement factor can be as high as 10^{14}, facilitating observation to single molecule level (Kim & Shin 2011).

Method

SERS technique is highly specific as it identifies molecules based on their vibrational fingerprints and thereby permits detection with high sensitivity (Pozzi *et al*. 2013). Essentially, SERS process involves three steps: preparation, measurement and detection. Preparation involves manufacturing of SERS-active substances and its adsorption to targeted molecules leading to enhanced Raman scattering. The measurement process relies on the sensitivity and specificity under energetic, temporal and spatial resolutions. Detection and data analysis involve acquisition of unique spectra of different molecules present in the sample (Ding *et al*. 2014).

Several studies have been conducted for the application of SERS in detecting adulterants in spices; especially with Sudan dye, considering its carcinogenic and mutagenic effects (Cheung *et al*. 2010; Gao *et al*. 2015; López *et al*. 2013). Di Anibal *et al*. (2012) compared different Raman spectroscopic modalities (Normal Raman, FT-Raman and SERS) and found that SERS is better suited for detection of Sudan I dye in culinary spices. A portable Raman spectrometer developed using SERS and multivariate chemometrics was used to provide quantitative data of Sudan I dye in spice products. The limit of detection was 48 $\mu g\ kg^{-1}$ of chilli powder and the substrate used was gold citrate reduced sol (Cheung *et al*. 2010). Similarly, Lopez *et al*. (2013) proposed a tool to detect Sudan I dye quantitatively, using electropolished aluminium as a substrate for SERS with low detection limits of $3x\ 10^{-7}$ M. Recently, a biosensor functioning using molecularly imprinted polymers, thin layer chromatography and SERS to detect Sudan I in paprika powder at levels as low as 1 ppm with gold colloid as SERS substrate has been fabricated. This biosensor exhibited rapidity in both separation (30-40 s) and detection (0.1-1 s) and can be used as an effective screening tool for Sudan I adulteration (Gao *et al*. 2015). To detect water insoluble dyes, in the presence of water soluble competitor, Jahn *et al.* (2015) developed a hydrophobic surface modified sensor layer on the SERS active substrate (enzymatically grown silver nanoparticles) and detected Sudan III adulterants upto concentration of 9 μmol/L in methanol extracted real food samples.

Fourier Transform-Infra Red Spectroscopy

Principle

Fourier transform-infra red spectroscopy (FT-IRS) is a rapid, non-destructive analytical technique used to detect adulterants in food products including spices. When chemical bonds with electric dipole moment interact with infrared radiation, they impart changes in the atomic

displacement, leading to natural vibrations at molecular level (Ferraro & Basile 2012). Such stretching and bending type vibrational effects can cause changes in the behaviour of different functional groups present in the sample, which in turn could be measured as they are unique for each material. The position and intensity of a spectrum gives the qualitative and quantitative information, respectively (Baker *et al*. 2014).

Method

In an FT-IR spectrometer, the monochromator is replaced with an interferometer which allows instantaneous passage of radiation of all wavelengths into the sample instead of filtering or dispersing them. Radiation from the source is allowed to strike a beam splitter, that reflects a portion of the radiation to a fixed mirror and transmits other portion to a movable mirror. Recombination of these radiations occurs at the beam splitter where either constructive or destructive interference takes place, determining the amount of light reaching the detector. Signal obtained at the detector in the form of a time-domain spectrum is converted to a frequency-domain spectrum by Fourier transformation (Ferraro & Krishnan 2012). Photon transducers measure the current produced by the energy obtained from the source. Since infrared radiation do not have sufficient energy to produce a measurable current, thermal transducers are used in FT-IR spectrometers (Harvey 2000; Kealey & Haines 2002).

FT-IRS as a method of analysis and quality control requires minimal or no sample preparation processes (Consonni *et al*. 2016). Karimi *et al*. (2016) successfully detected and quantified food colorants including Allura red, Azorubine, Quinoline yellow, Sudan II, Sunset yellow and Tartazinein saffron. Similarly, Dhakal *et al*. (2016) quantitatively evaluated different concentrations of metanil yellow in turmeric powder using FT-IRS and FT-Raman Spectroscopy. The FT-IR spectra of metanil yellow and turmeric powder (Fig. 2) shows peak at varying wavelengths because of variation in response of functional groups to IR radiation. For instance, the peak at 1140 cm^{-1} in metanil yellow is due to N=N site. After noise removal using a Savitzky-Golay filter the method can be used in authentication of spice oils. Importantly, there is reduced or near-zero use of hazardous solvents and reagents, making the approach 'green'. Nurrullhidayah *et al*. (2011) used FTIR to detect black cumin (*Nigella sativa* L.) seed oil adulterated with grape seed oil. In the spectra obtained, black cumin seed oil showed sharp peaks at 1117 and 1098 cm^{-1}, whilst grape seed oil showed peak at 1744 cm^{-1} only.

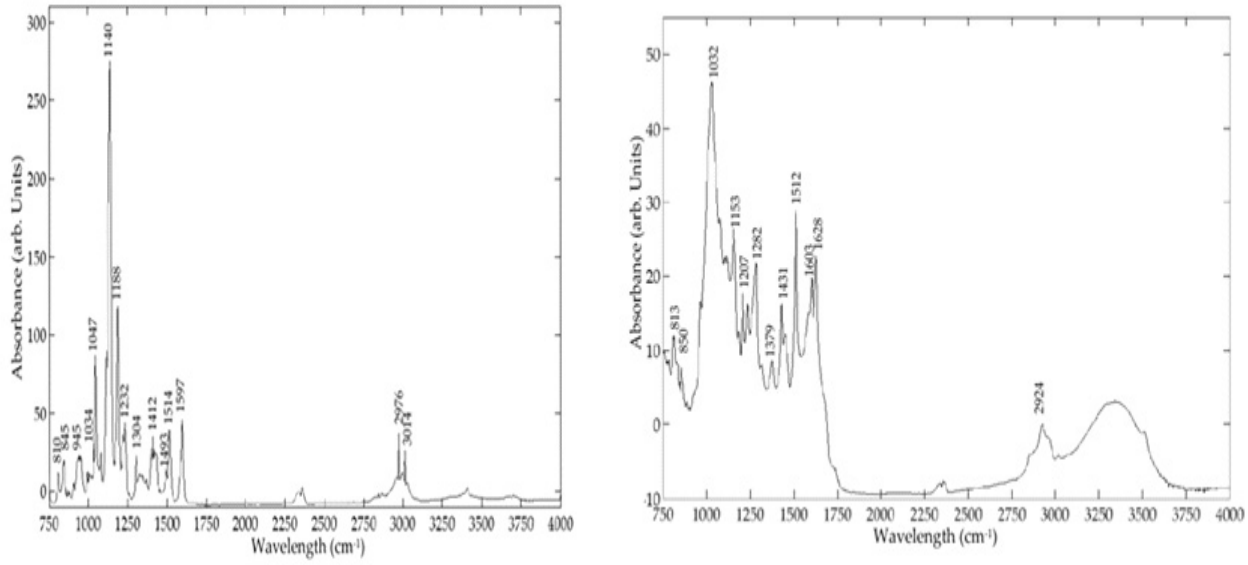


Fig. 2. FT-IR spectra of (A) Metanil yellow (B) Turmeric powder

(Reprinted with permission from Dhakal *et al*. (2016), MDPI journals)

Isotope Ratio Mass Spectroscopy

Principle

Isotope ratio mass spectroscopy (IRMS) as a unique technique in food authentication and quality control involves examining chemical and biological origins of a substance (Dong *et al*. 2018; Jiang *et al*. 2015; Potocnik *et al*. 2016). Isotopes are atoms that have same number of protons but varying number of neutrons. Variations in physico-chemical properties of isotopes, otherwise known as 'fractionation' or 'isotope effect' occur due to relatively higher vibrational energy of lower energy levels of heavier isotopes than that of lighter isotopes. Since rotational and translational energies of isotopes are more or less equal, molecular vibrations are the basis for IRMS (Sharp 2017). In any irreversible chemical reaction, the percentage of lighter isotopes formed as products is higher than that of heavier isotopes, as the latter require higher energy for chemical bonding. Variations in isotopic abundance of light elements like $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{2}D/^{1}H$, $^{15}N/^{14}N$ and $^{34}S/^{32}S$ are measured with reference to an isotopic standard using IRMS (Muccio & Jackson 2009).

Method

The major components of IRMS include a sample delivery system in which either the sample is combusted and transformed into gas using an elemental analyzer or a gas chromatography unit, an electron ionization source to ionize and accelerate the gas molecules, a magnetic sector to disperse mono-energetic ions of varying mass through the magnetic field, a faraday-collector to measure the current of each ion beam and a computer controlled data acquisition system to amplify and display values as digital output (Brand 2004; Kelly 2003; Novák *et al*. 2016).

In general, naturally occurring substances are enriched with lighter isotopes and the ratio of isotopes is considered to be unique to a substance and could indicate origin from a particular geographic location. Adulteration will alter this ratio. IRMS has been useful in authenticity control of spices and spice products such as essential oils (Frank *et al*. 1995; Greule *et al*. 2008). Gruele *et al*. (2010) used an IRMS approach for rapid detection of adulteration in vanillin by comparing the carbon and hydrogen stable isotope values of vanillin molecule and vanillin methoxyl groups of authentic and synthetic vanillin samples of different origin. This technique requires 1 mg and 4 mg of samples for stable carbon and stable hydrogen analysis, respectively. The approach can be used to control adulteration in vanilla; a serious concern, particularly to natural vanilla.

Proton Nuclear Magnetic Resonance Spectroscopy

Principle

Proton nuclear magnetic resonance spectroscopy (^{1}H-NMRS) technique focuses on identifying the molecular configuration of a sample. Generally a charged atomic nucleus spins in random directions by generating a magnetic field. When an external magnetic field is applied, nuclei get aligned in a direction along or against the direction of the external magnetic field. Accordingly, these nuclei will be in higher energy states (against the direction of external magnetic field) or lower energy states (along the direction of external magnetic field). When radiofrequency waves hit these molecules, flipping of nuclei between higher and lower energy states occur. During this process, electromagnetic waves are emitted and the NMR spectrometer detects these signals (Isengard & Breithaupt 2015).

^{1}H-NMRS has been widely used in quality control of spices like saffron, turmeric, paprika and curry and in the detection of adulterants, especially colorants and bulking agents (Di Anibal, Callao *et al.* 2011; Di Anibal, Ruisánchez *et al.* 2011; Petrakis *et al.* 2015; 2017). Di Anibal Callao *et al.* (2011) used information from UV-Vis and ^{1}H-NMRS for detection of Sudan dyes in culinary spices at three different concentration levels of 1.4, 3.6, 7.1 g kg^{-1}, and used a multivariate class approach for classification. The study revealed that data from the joint approach could be used efficiently for detecting banned Sudan dyes in spices.

Hyper Spectral Imaging

Principle

Hyper spectral imaging (HSI) combines both, conventional imaging and spectroscopic imaging, and has a wide application in food and agricultural product quality and safety analysis.

Essentially, HSI acquires both spatial and spectral features simultaneously (Liu *et al.* 2017; Lu & Chen 1999). Hyper spectral images are made up of a number of neighbouring wavebands for each spatial position of a sample being studied. Consequently, the spectrum obtained for each position acts as a fingerprint that helps in characterisation of the particular pixel in that position (Elmasry *et al.* 2012; Shaw & Manolakis 2002).

Method

A typical HSI system consists of an illumination source (usually tungsten halogen or LED source), an objective lens through which light waves get reflected from the sample that moves on a motorized stage, a spectrograph to separate the reflected light into its component wavelengths, a camera operated usually in conjunction with either charge coupled device or complementary metal oxide semiconductor sensors for two-dimensional image acquisition and a personal computer where two-dimensional images of the sample are stacked to form a three-dimensional hypercube (Gowen *et al.* 2007).

By using obtained physical and chemical characteristics from the HSI spectra, the presence of foreign matter or adulterants in food and agricultural products can be identified. Vermaak *et al*. (2014) suggested that short wave infrared (SWIR) hyperspectral imaging with chemometric data analysis can be used to detect adulteration in star anise (*Illicium verum*), a dried fruit used in the treatment of infant colic, with Japanese star anise (*Illicium anisatum*), an adulterant containing neurotoxic compounds. The technique has proven potential in quality analysis of bulk samples when conveyed through conveyor belt systems.

High Performance/ Pressure Liquid Chromatography

Principle

HPLC is based on the principle that different analytes behave differently with the stationary phase. Components of the analyte elute at different rates depending on factors like polarity, stationary-mobile phase interaction, ion exchange, size exclusion, liquid-solid adsorption and liquid-liquid partitioning (Isengard & Breithaupt 2015; Vermaak *et al*. 2014).

Method

In a High Performance/Pressure Liquid Chromatography (HPLC) system, the mobile phase carrying components of an analyte mixture (sample) flows through a stationary phase in a narrow and uniform column made of porous silica capillaries. Usually, the stationary phase is polar, whilst the mobile phase is non-polar. However, a reverse phase HPLC uses a non-polar stationary phase and a polar mobile phase. In food quality applications, reverse phase HPLC is preferred as polar components elute faster than non-polar components due to hydrophobic interactions. Presence of gas bubbles in the mobile phase may lead to distortion of detected signal. In order to remove gas bubbles prior to functioning, either a vacuum pump is used or the mobile phase sparged with an inert gas can be used (Kealey & Haines 2002). HPLC instrumentation consists of a reciprocating pump to maintain a constant flow of a mobile phase, a loop injector to disperse the sample in the mobile phase, a separating column to separate the components of the sample, a detector for quantitative determination of different constituents separated from the sample and a computer to display the results (Harvey 2000).

HPLC has been used not only in differentiation of varieties of spices (Priyanka *et al.* 2016) but also in detection of adulterants such as Sudan dyes, Para-red and Rhodamine-B (Ertaº *et al.* 2007; Fu *et al.* 2015). Tateo & Bononi (2004) used combination of HPLC and APCI-MS (Atmospheric Pressure Chemical Ionization – Mass Spectrometry) to detect and quantify Sudan I present in chillies. The study found that extracts from Sudan I from chilli added food products can be efficiently detected and quantified using HPLC and APCI-MS at very low concentrations. From Fig 3, it can be observed that sharper the peak, the more concentrated the component; whereas, wider peak indicates dispersed components. Though HPLC is an excellent choice for quantitative detection, time and cost requirements are high (Di Anibal *et al.* 2009).

Electronic-nose

Principle

Electronic-nose **(**E-nose) systems combined with

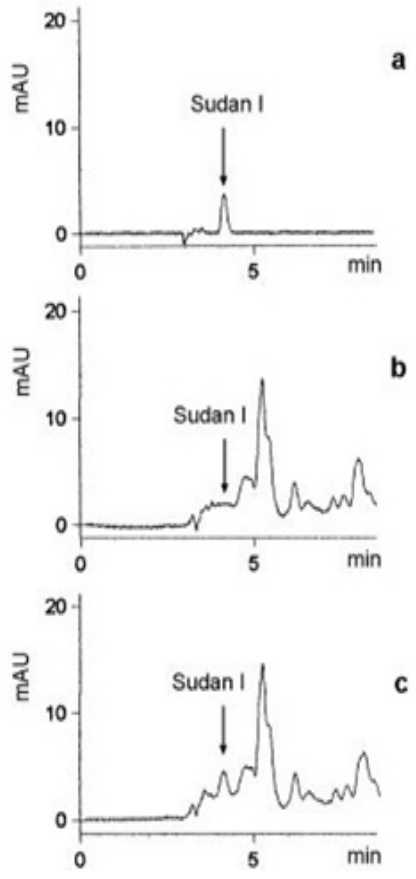


Fig 3. HPLC elution profile at ë = 481 nm of (a) Sudan I solution at 489 µg L^{-1} (b) ethanolic extract from "hot chilli" (c) ethanolic extract "hot chilli" at 391 µg L^{-1} enriched with Sudan I at 9.59 mg kg^{-1}

(Reprinted with permission from Tateo & Bononi (2004), American Chemical Society)

computerised data processing tools consist of an array of gas sensors that can mimic the olfactory function of human nose in various functional aspects. The approach provides higher degree of selectivity and specificity for detecting volatile compounds within the headspace region (Haddi *et al.* 2014). Chemical changes occur when volatiles come in contact with sensors and a transducer converts them to electrical signals whose totality is used in the multivariate analysis of detecting the sample by pattern recognition (De Vito *et al.* 2015).

Method

An e-nose consists of a sample delivery system which absorbs volatiles from the sample to be analysed, a detection system and a computing system. The detection system consists of sensors which can be broadly classified as hot sensors (eg: Metal oxide semiconductors and metal oxide semiconducting field effect transistor) and cold sensors (eg: Conducting polymers, oscillating sensors, optical or electrochemical sensors) based on operating temperature range (Haugen 2001). An important component of an e-nose system is the data processing unit, operated using principal component analysis, partial least squares, functional discriminant analysis, hierarchical cluster analysis, fuzzy logic or artificial neural network algorithms (Omatu & Yano 2016). Neural networks operate on the basis of functional mapping between known and unknown samples. Information processing in an e-nose is done along a number of input and hidden layers that are grouped on the basis of similarities and differences to give a single digital output (Adak & Yumusak 2016).

E-nose systems can be used in quality monitoring of food products; especially in spices, where aroma, flavor and color are of prime concern (Leela *et al*. 2017). Kukade *et al.* (2014) successfully used e-nose to classify three spice oils (cardamom, nutmeg and clove oil) with classification accuracy of around 97.1%. Recently, Heidarbeigi *et al.* (2015) demonstrated detection of saffron adulteration with safflower and corn stigma. E-nose, containing MOS (Metal Oxide Semiconductors) sensors, successfully yielded aroma fingerprints of the pure compound and the adulterated compounds. Obtained features were analysed with principal component analysis and artificial neural network and it was found that e-nose could provide classification accuracies of 100% and 86.87% for original saffron and other adulterants, respectively.

The concern over safety and authenticity of spices has resulted in establishing higher standards for quality evaluation and improved methods to function at various stages of post-harvest, storage and shipment. Though development of various analytical tools employed, standardization and authentication of spice products have increased. Besides adulterants, the quality of spice is lost due to the presence of contaminants, filth matter or microbial toxic substances like aflatoxin, mycotoxins and heavy metals like lead, cobalt,

chromium, uranium. These foreign materials could be detected by techniques like inductively coupled plasma-mass spectrometry, x-ray fluorescence, neutron activation analysis, graphite furnace atomic absorption spectroscopy, graphite furnace atomic emission spectroscopy, flame atomic absorption spectroscopy and flame atomic emission spectroscopy. Further techniques like IRMS, NMRS, FT-IRS acts as a fingerprinting tool to effectively detect adulteration of spices and spice products even at trace levels; including the position of adulterant at molecular level and global characterization. However, the major drawbacks in these technologies are their establishment and running cost. This could be overcome by the use of electronic sensors, but their sensitivity to different chemical compounds relies on numerous factors. Thus the robustness of all analytical techniques in detecting adulterants discussed in this review could be enhanced to a higher level with the combination of chemometric tools.

References

Adak M & Yumusak N 2016 Classification of e-nose aroma data of four fruit types by abc-based neural network. Sensors 16: 304.

Alice J, Sujeetha R P, Moses J A, Loganathan M & Meenatchi R 2016 Hermetic Storage of Turmeric Rhizomes. Adv. Life Sci. 5: 3174-3178.

Baker M J, Trevisan J, Bassan P, Bhargava R, Butler H J, Dorling K M & Fielden P R 2014 Using Fourier transform IR spectroscopy to analyze biological materials. Nat Protoc. 9: 1771-1791.

Bharath K S, Maria L M, Moses J A & Anandharamakrishnan C 2017 Green Synthesis of Metal Nanoparticles using Spices. Cut Edge. 3: 42-45.

Brand W A 2004 Mass spectrometer hardware for analyzing stable isotope ratios. In: De Groot P A (Ed.) Handbook of Stable Isotope Analytical Techniques. Vol. 1. (pp.835–856). Elsevier, Amsterdam.

Cheung W, Shadi I T, Xu Y & Goodacre R 2010 Quantitative analysis of the banned food dye sudan-1 using surface enhanced raman scattering with multivariate chemometrics. J. Phys. Chem. C. 114: 7285-7290.

Consonni R, Ordoudi S A, Cagliani L R, Tsiangali M & Tsimidou M Z 2016 On the traceability of commercial saffron samples using 1H-NMR and FT-IR metabolomics. Molecules 21: 1-13.

De Vito S, Salvato M, Massera E, Miglietta M, Fattoruso G & Di Francia G 2015 Advanced pattern recognition techniques for fast and reliable e-nose response analysis in NDTs scenarios. In: Compagnone D, Baldini F, Di Natale C, Betta G & Siciliano P (Eds.) Sensors (pp.235–240). Springer, New York.

Dhakal S, Chao K, Schmidt W, Qin J, Kim M & Chan D 2016 Evaluation of Turmeric Powder Adulterated with Metanil Yellow Using FT-Raman and FT-IR Spectroscopy. Foods 5: 36.

Dhanya K, Syamkumar S & Sasikumar B 2009 Development and application of SCAR marker for the detection of papaya seed adulteration in traded black pepper powder. Food Biotechnol 23: 97-106.

Dhanya K, Syamkumar S, Jaleel K & Sasikumar B 2008 Random amplified polymorphic DNA technique for detection of plant based adulterants. J. Spices Arom. Crops 17: 75-81.

Dhanya K, Syamkumar S, Siju S & Sasikumar B 2011a SCAR markers for adulterant detection in ground chilli. Br. Food J. 113: 656-668.

Dhanya K, Syamkumar S, Siju S & Sasikumar B 2011b Sequence characterized amplified region markers: A reliable tool for adulterant detection in turmeric powder. Food Res. Int. 44: 2889-2895.

Di Anibal C V, Callao M P & Ruisánchez I 2011 1H NMR and UV-visible data fusion for determining Sudan dyes in culinary spices. Talanta. 84: 829-833.

Di Anibal C V, Odena M, Ruisánchez I & Callao M P 2009 Determining the adulteration of spices with Sudan I-II-II-IV dyes by UV-visible spectroscopy and multivariate classification techniques. Talanta. 79: 887-892.

Di Anibal C V, Rodriguez M S & Albertengo L 2014 UV-Visible spectroscopy and multivariate classification as a screening tool to identify adulteration of culinary spices with Sudan I and blends of Sudan I + IV dyes. Food Anal. Methods 7: 1090-1096.

Di Anibal C V, Ruisánchez I & Callao M P 2011 High-resolution 1H Nuclear Magnetic Resonance spectrometry combined with chemometric treatment to identify adulteration of culinary spices with Sudan dyes. Food Chem. 124: 1139-1145.

Di Anibal, C V, Ruisánchez I, Fernández M, Forteza R, Cerdà V & Callao M P 2012 Standardization of UV-visible data in a food adulteration classification problem. Food Chem. 134: 2326-2331.

Ding S Y, Zhang X M, Ren B & Tian Z Q 2014 Surface-Enhanced Raman Spectroscopy (SERS): General Introduction. In: Meyers R A (Ed.) Encyclopedia of Analytical Chemistry (pp.1–34). Wiley, New York.

Dong H, Xiao K, Xian Y & Wu Y 2018 Authenticity determination of honeys with non-extractable proteins by means of elemental analyzer (EA) and liquid chromatography (LC) coupled to isotope ratio mass spectroscopy (IRMS). Food Chem. 240: 717-724.

Elmasry G, Kamruzzaman M, Sun D W & Allen P 2012 Principles and applications of hyperspectral imaging in quality evaluation of agro-food products: A Review. Crit. Rev. Food Sci. Nutr. 52: 999-1023.

Ertaº E, Özer H & Alasalvar C 2007 A rapid HPLC method for determination of Sudan dyes and Para Red in red chilli pepper. Food Chem. 105: 756-760.

Ferraro J R & Basile L J 2012 Fourier transform infrared spectra: Applications to chemical systems. Academic press, London.

Ferraro J R & Krishnan K (Ed.) 2012 Practical fourier transform infrared spectroscopy: Industrial and laboratory chemical analysis. Elsevier, California.

Frank C, Dietrich A Kremer U & Mosandl A 1995 GC-IRMS in the authenticity control of the essential oil of *Coriandrum sativum* L. J. Agri. Food Chem. 43: 1634-1637.

Fu D S, Wu P P, Zhong X D, Liu Q, Luo H D & Li Y Q 2015 A simple synchronous fluorescence approach for rapid and sensitive determination of Rhodamine B in chilli products. Food Anal. Methods 8: 189-194.

Gao F, Hu Y, Chen D, Li-Chan E C Y, Grant E & Lu X 2015 Determination of Sudan I in paprika powder by molecularly imprinted polymers-thin layer chromatography-surface enhanced Raman spectroscopic biosensor. Talanta. 143: 344-352.

Gowen A A, O'Donnell C P, Cullen P J, Downey G & Frias J M 2007 Hyperspectral imaging – an emerging process analytical tool for food quality and safety control. Trends Food Sci. Technol. 18: 590-598.

Greule M, Hänsel C, Bauermann U & Mosandl A 2008 Feed additives: authenticity assessment using multicomponent-/multielement-isotope ratio mass spectrometry. Eur. Food Res. Technol. 227: 767-776.

Greule M, Tumino L D, Kronewald T, Hener, Schleucher J, Mosandl A & Keppler F 2010 Improved rapid authentication of vanillin using ä13C and ä2H values. Eur. Food Res. Technol. 231: 933-941.

Haddi Z, Mabrouk S, Bougrini M, Tahri K, Sghaier K, Barhoumi H, Bari N E, Maaref A, Jaffrezic-Renault N & Bouchikhi B 2014 E-Nose and E-Tongue combination for improved recognition of fruit juice samples. Food Chem. 150: 246-253.

Harvey D 2000 Modern analytical chemistry. Vol. 381. McGraw-Hill, New York.

Haugen J E 2001 Electronic noses in food analysis. In: Klein B P (Ed.) Headspace analysis of foods and flavors (pp.43–57). Springer, US.

Heidarbeigi K, Mohtasebi S S, Foroughirad A, Ghasemi-Varnamkhasti M, Rafiee S & Rezaei K 2015 Detection of adulteration in saffron samples using electronic nose. Int. J. Food Prop. 18: 1391-1401.

Isengard H D & Breithaupt D 2015 Food Analysis. In: Platt G C (Ed.) Food science and technology (pp.33–56). Blackwell, New Jersy.

Jahn, M, Patze S, Bocklitz T, Weber K, Cialla-May D & Popp J 2015 Towards SERS based applications in food analytics: Lipophilic sensor layers for the detection of Sudan III in food matrices. Analytica chimica acta 860: 43-50.

Jiang C, Cao L, Yuan Y, Chen M, Jin Y & Huang L 2014 Barcoding melting curve analysis for rapid, sensitive and discriminating authentication of Saffron (*Crocus sativus* L.) from its adulterants. Biomed Res. Int. 1-10.

Jiang W, Xue J, Liu X, Wang D, Guo Y & Wang L 2015 The application of SNIF-NMR and IRMS combined with C, H and O isotopes for detecting the geographical origin of Chinese wines. Int. J. Food Sci. Technol. 50: 774-781.

Karimi S, Feizy J, Mehrjo F & Farrokhnia M 2016 Detection and quantification of food colorant adulteration in saffron sample using chemometric analysis of FT-IR spectra. RSC Adv. 6: 23085-23093.

Kealey D & Haines P J 2002 Instant notes. Anal. Chem. 270-280.

Kelly S 2003 Using stable isotope ratio mass spectrometry (IRMS) in food authentication and traceability. Food Authent. Traceability. 156–183.

Kerker M 2016 The scattering of light and other electromagnetic radiation. Elsevier, New York.

Kim K & Shin K S 2011 Surface-enhanced Raman scattering: a powerful tool for chemical identification. Anal. Sci. 27: 775-783.

Kojoma M, Kurihara K, Yamada K, Sekita S, Satake M & Iida O 2002 Genetic identification of cinnamon (*Cinnamomum* spp.) based on the trnL-trnF chloroplast DNA. Planta Med. 68: 94-96.

Kukade M V, Moshayedi A J & Gharpure D C 2014 Electronic-nose (E-nose) for recognition of Cardamom, Nutmeg and Clove oil odor. Electron its Interdiscip Appl. (NCAEIA - 2014).

Leela N K, Muneeb A M, Mukherjee S, Ghosh D & Bhattacharya N 2017 Essential oil content of cardamom (*Elettaria cardamomum* Maton) by Hand-held Electronic Nose. J. Spices Arom. Crops 26: 131-135.

Liu Y, Pu H, & Sun D W 2017 Hyperspectral imaging technique for evaluating food quality and safety during various processes: A review of recent applications. Trends Food Sci. Technol. 69: 25-35.

López M I, Ruisánchez I & Callao M P 2013 Figures of merit of a SERS method for Sudan I determination at traces levels. Spectrochim Acta - Part A Mol Biomol. Spectrosc. 111: 237-241.

Lu R & Chen Y 1999 Hyperspectral imaging for safety inspection of food and agricultural products. Proc. SPIE. 3544: 121-133.

Manning L & Soon J M 2014 Developing systems to control food adulteration. Food Policy 49: 23-32.

Marieschi M, Torelli A & Bruni R 2012 Quality control of saffron (*Crocus sativus* L.): Development of SCAR markers for the detection of plant adulterants used as bulking agents. J. Agri. Food Chem. 60: 10998-11004.

McNaught A D & Wilkinson A 1997 Compendium of chemical terminology. Vol. 1669. Oxford: Blackwell Science, New Jersey.

Moses J A, Alagusundaram K & Kavitha C V 2014 Curing and drying of cardamom. Processed Food Industry. 10: 21-28.

Muccio Z & Jackson G P 2009 Isotope ratio mass spectrometry. Analyst 134: 213-222.

Novák V, Dendisov M, Matìjka P & Bouø P 2016 Explanation of surface-enhanced raman scattering intensities of p-aminobenzenethiol by density functional computations. J. Phys. Chem. C. 120: 18275-18280.

Nurrulhidayah A F, Che Man Y B, Al-Kahtani H A & Rohman A 2011 Application of FTIR spectroscopy coupled with chemometrics for authentication of *Nigella sativa* seed oil. Spectroscopy 25: 243-250.

Omatu S & Yano M 2016 E-nose system by using neural networks. Neurocomputing. 172: 394-398.

Otto M 2016 Chemometrics: Statistics and computer application in analytical chemistry. John Wiley & Sons, New Jersey.

Parvathy V A, Swetha V P, Sheeja T E & Sasikumar B 2015 Detection of plant-based adulterants in turmeric powder using DNA barcoding. Pharm Biol. 53: 1774-1779.

Parvathy V A, Swetha V P, Sheeja T E, Leela N K, Chempakam B & Sasikumar B 2014 DNA barcoding to detect chilli adulteration in traded black pepper powder. Food Biotechnol. 28: 25-40.

Penner M H 2017 Basic principles of spectroscopy. In: Food analysis (pp.79–88) Springer, Cham.

Peter K V & Zachariah T J 2000 Quality assurance in spices and spice products-modern methods of analysis. J. Spices Arom. Crops 9: 79.

Petrakis E A, Cagliani L R, Polissiou M G & Consonni R 2015 Evaluation of saffron (*Crocus sativus* L.) adulteration with plant adulterants by 1H NMR metabolite fingerprinting. Food Chem. 173: 890-896.

Petrakis E A, Cagliani L R, Tarantilis P A, Polissiou M G & Consonni R 2017 Sudan dyes in adulterated saffron (*Crocus sativus* L.): Identification and quantification by 1H NMR. Food Chem. 217: 418-424.

Potocnik T, Ogrinc N, Potocnik D & Kosir I J 2016 Fatty acid composition and ä13C isotopic ratio characterisation of pumpkin seed oil. J. Food Compos Anal. 53: 85-90.

Pozzi F, Porcinai S, Lombardi J R & Leona M 2013 Statistical methods and library search approaches for fast and reliable identification of dyes using surface-enhanced Raman spectroscopy (SERS). Anal. Methods 5: 4205.

Priyanka R, Vasundhara M, Jayaram A & Nuthan D 2016 A study on curcuminoid profile of *Curcuma longa* L. varieties as affected by processing method. J. Spices Arom. Crops 25: 26-33.

Sharp Z 2017 Principles of Stable Isotope Geochemistry.

Shaw G & Manolakis D 2002 Signal processing for hyperspectral image exploitation. IEEE Signal Process Mag. 19: 12-16.

Silvis I C J, Van R S M, Van der F H J & Luning P A 2017 Assessment of food fraud vulnerability in the spices chain: An explorative study. Food Control. 81: 80-87.

Skoog D A, Holler F J & Crouch S R 2017 Principles of instrumental analysis. Cengage learning.

Spice Board of India 2017 Ministry of Commerce and Industry, Cochin, India. http://www.indianspices.com/

Swetha V P, Parvathy V A, Sheeja T E & Sasikumar B 2014 DNA Barcoding for Discriminating the Economically Important *Cinnamomum verum* from Its Adulterants. Food Biotechnol. 28: 183-194.

Swinehart D F 1962 The beer-lambert law. J. Chem. Edu. 39: 333.

Tateo F & Bononi M 2004 Fast determination of Sudan I by HPLC/APCI-MS in hot chilli, spices, and oven-baked foods. J. Agri. Food Chem. 52: 655-658.

Toteja G S, Mukherjee A, Mittal R & Saxena B N 1990 Manual methods of analysis for adulterants and contaminants in foods. Indian Counc. Med. Res.

Vermaak I, Viljoen A & Lindström S W 2014 Hyperspectral imaging in the quality control of herbal medicines - The case of neurotoxic Japanese star anise. J. Pharm. Biomed Anal. 75: 207-213.