The Use of FTIR Spectroscopy Combined with Multivariate Analysis in Food Composition Analysis

2

Gunawan Indrayanto and Abdul Rohman

Abstract

Infrared spectroscopy, one of the vibrational spectroscopies, has emerged as rapid and powerful analytical technique for identification and quantitative analysis of food component. FTIR spectra is fingerprint analytical technique, therefore, by selecting the specific region, some analytical purposes can be achieved such as identification, confirmation and quantitative analysis of analyte(s) of interest in food samples. Equipped with some sampling technique such as attenuated total reflectance and combined with chemometrics software such as principal component analysis for classification and multivariate calibration for multicomponent analysis, FTIR spectroscopy has been successfully used for compositional analysis of food. The method is rapid with minimum or without sample preparation and is not involving the extensive solvents and reagents.

Keywords

FTIR spectroscopy · Food composition · Fingerprint technique · Chemometrics · Authentication analysis

G. Indrayanto
Faculty of Pharmacy, Universitas Surabaya, Surabaya, East Java, Indonesia

A. Rohman (✉)
Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Universitas Gadjah Mada, Yogyakarta, Indonesia
e-mail: abdul_kimfar@ugm.ac.id

A. K. Shukla (ed.), *Spectroscopic Techniques & Artificial Intelligence for Food and Beverage Analysis*, https://doi.org/10.1007/978-981-15-6495-6_2

2.1 Introduction

Infrared (IR) spectroscopy is analytical technique related to interaction studies between analytes and electromagnetic radiation. This interaction can be in the form of transmission, absorption, scattering and reflection of light due to incident light in the spectral range corresponding to infrared region into samples. The frequencies or wavelengths, at which the samples absorb IR radiation and their corresponding intensities (either transmittance or absorbance), are recorded into IR spectrum [1]. IR spectroscopy is the most vibrational spectroscopic techniques widely applied in food analysis [2], which measure the vibrational energy levels in a compound [3]. IR spectroscopy is one of fingerprint analytical techniques, commonly applied in wide application in food science. Fourier transform infrared (FTIR) spectroscopy is an ideal technique for characterization and identification, confirmation, and quantitative analysis of food components [4].

There are two types of spectrometer, namely dispersive instrument and Fourier-transformed spectrophotometer based on interferometer. FTIR spectroscopy offer some advantages in identification and quantitative analyses including fast spectral data acquisition, without or minimal sample preparation, non-destructive in which the analysed samples by FTIR spectroscopy can be analysed using other methods like chromatographic-based techniques, high-throughput, low cost, applicable for a wide range of physical sample types (liquid, semi-solid and solid samples). Besides, IR spectroscopy can be used for analysis of multiple analytes, especially in combination with multivariate analysis [5]. FTIR spectroscopy can be used in the wide range of wavenumbers region which provide excellent resolution of spectra along with the large number of peaks, which can be correlated with the presence of certain analytes in the samples [6]. Due to its versatility with minimum use of solvents, FTIR spectroscopy is considered as green analytical techniques which are more environmentally friendly [7].

However, FTIR spectroscopy also has some drawbacks. The environment condition could affect the nature of spectra, therefore the temperature and humidity must be controlled. The FTIR spectra may vary which make the spectral interpretation more complicated [8]. The spectral data obtained are frequently complex which need sophisticated statistical tools known as chemometrics. The advance development of multivariate calibration can assist the resolving unique spectral patterns, improving instrument sensitivity, and monitoring the analyte characteristics in the analysed samples [9].

2.2 Infrared Spectroscopy

In analytical chemistry, infrared spectroscopy is considered as powerful technique for analysing inorganic and organic samples, in the form of gases, liquids, and solids either qualitatively or quantitatively. IR spectroscopy is based on the vibrations (stretching or bending) of chemical bonds within the molecules at specific frequen-

cies. The vibrations can be described by the laws of physics (Hooke laws). The chemical bonds can absorb IR radiation; they are excited to a higher energy level which make the vibration of bonds at specific frequency. At ambient temperature, molecules are in the levels of zero energy [10].

The region of IR radiation can be categorized in three regions, near-infrared (NIR), mid-infrared (MIR) and far-infrared (FIR). NIR corresponds to wavenumbers of 14,000–4000 cm^{-1} (or wavelength of 800–2500 nm), MIR corresponds to 4000–400 cm^{-1} (or wavelength 2500–50,000 nm) and FIR corresponds to 400–50 cm^{-1} (or wavelength 50,000–1,000,000 nm). Among these regions, MIR is the most widely used for the analytical purposes including qualitative analysis, confirmation and quantitative analyses of food composition within the analysed samples [11]. FTIR spectra are fingerprint spectra and can be used to characterize the chemical compounds. FTIR spectra can be obtained using the modes of absorbance or transmittance. The energy at any peak in IR spectrum corresponds to the vibrational frequency of functional groups present in the sample molecule [12].

2.2.1 Infrared Absorption Process

IR spectroscopy is mainly related to the molecular vibrations. The molecular absorption of EMR in IR region can cause the transition between the ground (lowest) state and the rotational and vibrational energy levels in the molecules [13]. As other absorption processes in spectroscopic techniques, the absorption of IR radiation is *a quantized process*, meaning that functional groups in molecule samples only absorbed IR radiation at selected frequencies (energies) which corresponds to energy changes in the order of 2–10 kcal/mol. Radiation in this range corresponds to the stretching and bending vibrations of the chemical bonds in the most covalent molecules [1], corresponding to the energy levels of chemical bonds. According to Hooke's law, the frequencies of stretching and bending vibrations are affected by (a) the mass of the atoms, in which the higher the mass the lower the frequency, (b) the geometrical shape of the molecules, (c) the bonds stiffness and (d) the periods of the associated vibrational coupling.

To absorb IR radiation, bonds in the molecule must have dipole moment such as CH_2. The modes of vibration can be either stretching (change in bond length) or bending (change in bond angle). Stretching can be symmetrical (in plane) or asymmetrical (out of plane), and the bending vibration is identified as rock or deformation when moved in the same or in opposite direction, respectively [14]. Figure 2.1 illustrates the vibration modes of methylene ($–CH_2–$) group. The modes of vibration can be either stretching (in which bond length is observed) or bending (in which bond angle is changed). Stretching can be symmetrical (in plane) or asymmetrical (out of plane). The bending vibration is identified as rock or deformation when moved in the same or in opposite direction, respectively. The modes of vibration can be either stretching (in which bond length is observed) or bending (in which bond angle is changed). Stretching can be symmetrical (in

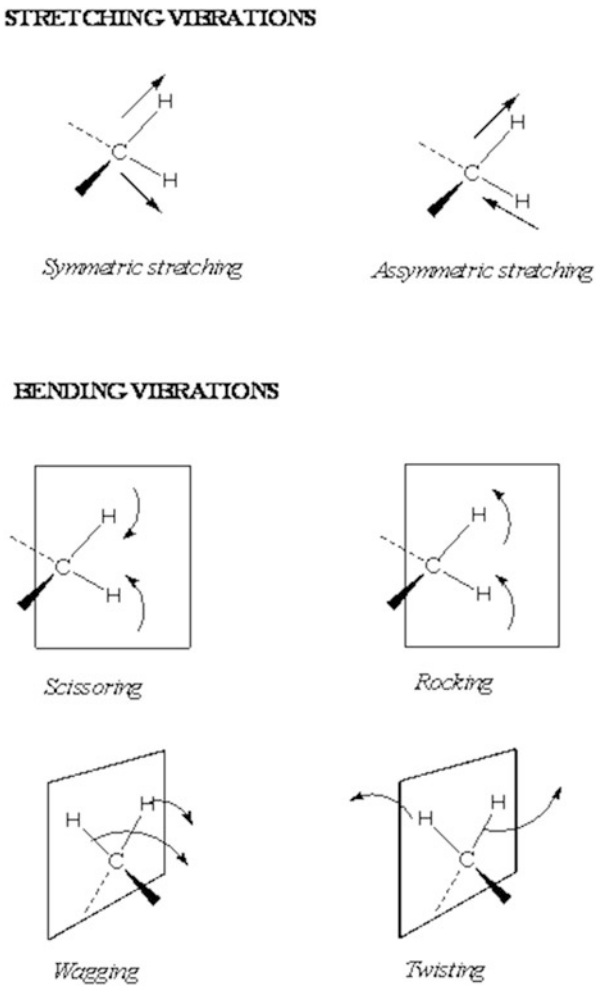

Fig. 2.1 The vibration modes (stretching and bending) in CH_2 group. Adapted from [1]

plane) or asymmetrical (out of plane). The bending vibration is identified as rock or deformation when moved in the same or in opposite direction, respectively [15].

2.2.2 Instrumentation

The instrument systems of infrared spectrometers can be in the form of dispersive and Fourier-transformed using interferometer [16]. The dispersive type has not been widely used in chemical analyses because some difficulties were met in sample handling. Dispersive instrument is also not equipped with software to treat the

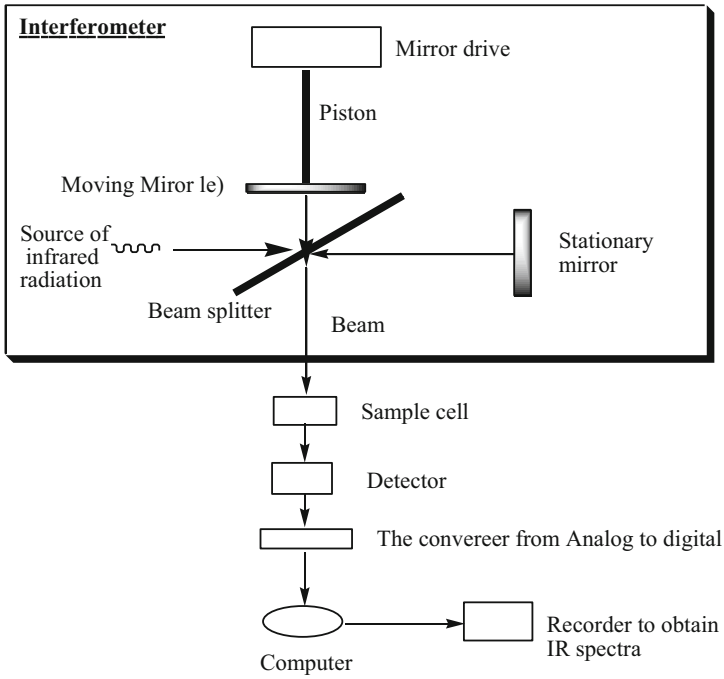

Fig. 2.2 Schematic of FTIR spectrophotometer. Adapted from [20]

spectral acquisition and processing systems. Therefore, in the last decades, FTIR instrument has replaced dispersive instrument and has appeared to become an important method for certain analytical purposes [17].

FTIR spectrophotometers are based on interferometer, therefore, they differ fundamentally from dispersive spectrometer. The Michelson interferometer is typically used in most FTIR spectrophotometers (Fig. 2.2). Michelson interferometer is normally composed of two mirrors, namely moving mirror and stationary mirror. In interferometer, the moving mirror will travel at constant velocity. The beam splitter made from KBr coated with Ge is located between two mirrors [18]. Beam splitter will divide the radiation beam into two parts, one part will be transmitted into a moving mirror while the part one is reflected into stationary mirror. When the radiation beams are reflected back, they will recombine to produce constructive/destructive interference patterns. After the IR energy has been selectively absorbed by a sample located between the beam splitter and the detector, the fluctuations in the energy intensities will reach to detector and then will be digitalized in real time, yielding an interferogram [19].

The obtained interferogram encompasses all requisite information during FTIR spectra of the analysed sample; however, interferogram outputs are in the time domain. The interferogram in time domain is then converted to frequency domain

using Fourier transformation for producing conventional FTIR spectrum. Fourier transformation is a mathematical algorithm typically applied during the decoding interferogram to obtain interpretable information related to individual frequencies in FTIR spectrum. Wavelength accuracy is necessary in order to obtain correct and highly resolved spectra. It is dependent on knowing the exact position of the moving mirror and is achieved using an internal reference laser (He-Ne), which monitors the position of the moving mirror during the scan. This leads to the precise scanning and to accurate spectrum collection in relation to the wavelength position, which is a key determinant for quantitative spectroscopy [1].

Because of its rapidity in scanning of FTIR spectra and its capability to provide sensitive response, FTIR spectrophotometers are the instrument choice for analysis of samples. FTIR instruments have distinct advantages over dispersive spectrometers, namely: (a) Fellgett advantage capable of providing better speed and sensitivity; (b) Jacquinot advantage by increasing the optical throughput; (c) dispersion or filtering of slits is not needed; (d) Connes advantage as shown by the presence of internal laser reference; (e) simpler mechanical design; (f) the contributions of stray light and light emission are eliminated and (g) FTIR instrument is easily connected and compatible with powerful data recording [21]. The significant advantage of FTIR instrument is the multiplexing advantage, in which all frequencies corresponding to absorption of chemical bonds can be measured simultaneously, as a consequence, whole FTIR spectra of analysed samples can be obtained in a single scanning. In addition, the signal of FTIR spectrophotometer has excellent sensitivity as indicated by higher ratio of signal to noise (S/N) that of dispersive instrument. Another important factor in the success of FTIR spectroscopy is the sophisticated software of chemometrics included in the instrument which facilitates spectral scanning and spectral treatments like derivatization and smoothing.

2.2.3 Sampling Preparation Techniques for Infrared Spectroscopy

Because of the large diversity of uses of IR spectroscopy in analysing and characterizing of food samples, a large number of sample preparation techniques have been developed and marketed over the years. Different sampling techniques have been used for obtaining better quality spectra, and new sensitive techniques have been developed and used in order to evaluate previously intractable samples. They can be divided into a few categories, namely transmission, internal reflectance, external reflectance, diffuse reflectance, photoacoustic detection and gas chromatography-infrared (GC/IR) [22]. According to USP 42 general method <854> Mid-Infrared Spectroscopy [23], the most common sample preparation techniques for FT-IR spectroscopy are by using potassium bromide disk, mineral oil mulls, self-supported polymer film, capillary film, liquid and solutions in transmission cells, gases, attenuated total reflectance, diffuse reflection and microscope sampling. In principle those techniques can be separated into transmission-, attenuated total reflectance (ATR)-, and diffuse reflectance-technique [24].

2.2.3.1 Transmission Technique

By transmission technique, the sample is placed precisely into sample holder. IR beam is passed through the holder containing the analysed samples, and the transmitted light is detected and recorded as IR spectrum. Samples should be first prepared as pellet, mull and film, before the measurement can be performed. The transmission techniques can be used alone, or in combination or with using accessories e.g. liquid-, gas-cells, microscope or gas chromatography. Many types of samples such as solid powders, liquids, gas, polymer film, can be analysed by using this technique [24]. Powdered organic and inorganic sample (1–2 mg) should be well mixed with 150 mg alkali halide (e.g. potassium bromide, potassium chloride and caesium iodide), finely pulverized to get homogenous mixture, and put in die to get pellet. In order to get transparent pellets, a power of around 8 tons is applied under a vacuum of several mmHg for several minutes. The pellet is then inserted into a sample holder in the spectrometer for analysis [23, 25, 26]. For preparing mull, 10–20 mg sample were pulverized in mortar then grinded with saturated hydrocarbon mineral oil (liquid paraffin, Nujol), to obtain a suspension, then the suspension was transferred into the cell (potassium bromide, sodium chloride, silver bromide or caesium iodide). Liquid paraffin exhibits absorption near 3000–2800 cm, 1460 cm, 1375 cm and 730 cm. Liquid sample can be measured by dropping it into the transmission cell, while gaseous sample can be analysed by the gas cell. Sample as thin film can be prepared by either melting or dissolved by solvents; this thin film method usually is used for analysing the polymers [27]. FT-IR spectrophotometer can be connected to a GC-IR module that contains liquid-nitrogen cooled MCT-A detector for performing GC-FT-IR analysis [28].

Some advantages of the transmission method are economical, well established, excellent spectral information and can well applied for quantitative work [24]. The disadvantages of transmission method that generally using alkali halide pellets or cells are hygroscopic; it needs skilled analyst and time consuming for preparing, liquid cells need to be filled without air bubble, homogenization of sample and alkali halide is difficult to achieve for some substances/materials like rubbers or other elastomers [29]. The other limitation of this technique is related to the sample thickness (except for gaseous samples), because the amount of IR energy absorbed by the sample is proportional to its thickness. Consequently, beyond a certain thickness, the sample will not transmit any IR radiation in the regions of the spectrum where it is strongly absorbing; therefore, no signal will reach the detector. The thickness is arranged in such a way that gives the absorbance value of 0.1–0.8 [30]. In order to overcome those disadvantages, a relatively new method of attenuated total reflectance (ATR) mode has been developed.

2.2.3.2 Attenuated Total Reflectance

For its simplicity, the sampling technique of ATR is widely used for analysis of the analysed samples. ATR is considered as one type of Internal Reflection Spectroscopy (IRS). The sample is positioned in good contact against special ATR crystal called an internal reflectance element (IRE) [31]. The basic principle of ATR

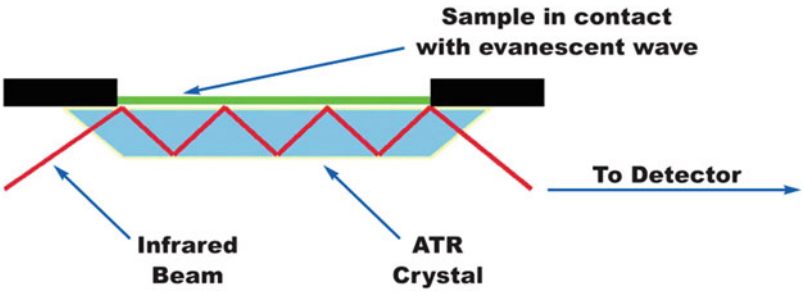

Fig. 2.3 A multiple reflection of attenuated total reflectance (ATR) system. (Courtesy of PerkinElmer, Shelton, CT 06484, USA) [29]

is shown in Fig. 2.3. An infrared beam enters the ATR crystal which has high refractive index at certain angle (usually 45°). The fraction of the light wave that reaches into the sample is called the evanescent wave. This wave will penetrate only a few microns (0.5–5 μ) beyond the crystal surface and then penetrate into the sample. In those spectral regions, the evanescent wave will be attenuated due to absorption of IR light by the analysed sample. After multiple internal reflections, the IR beam exits from the crystal and is then directed into the detector and recorded to get IR spectra. The system then produces an absorption infrared spectrum. During ATR scanning, the sample must be in good contact with ATR crystal surface. All sorts of samples can be placed directly on the surface of an ATR crystal, afterward measurements can be directly performed, and typically it needs only within seconds [29]. In order to attain the success of ATR, some conditions must be fulfilled namely [1] the sample must be on direct contact with ATR crystal, because the evanescent wave or bubble only extends beyond the crystal of 0.5–5 μ and [2] the refractive index of ATR crystal must be higher than that of the analysed sample. Usually, refractive index values of ATR crystals are between 2.38 and 4.01 at 2000 cm^{-1} [32].

There are some common crystals materials for ATR i.e. zinc selenide (ZnSe), germanium (Ge), silicon, diamond and KRS-5 (thallium iodide or thallium bromide). ZnSe (refractive index 2.43; spectral range 20,000–500 cm^{-1}) is a relatively low-cost ATR crystal and is perfect for analysing liquids and soft sample (gels). ZnSe can be used between pH 5 to pH 9. Due to relatively easily to scratches of the ZnSe crystal, care must be taken when cleaning it. Germanium (refractive index 4.01; spectral range 5000–600 cm^{-1}) is used to analyse highly absorbing samples like carbon-black coloured rubbers. Ge has a much better working pH range. Ge can be used for analysing weak acids and alkalis. Diamond (refractive index 2.40; spectral range 40,000–100 cm^{-1}) is the best ATR crystal material due to is robustness and chemically inert. The drawback of diamond is relatively more expensive compared to two other crystals. The ATR crystal must be always cleaned, usually by using a solvent soaked in piece of tissue (MeOH, Water, Isopropanol) [29, 33].

ATR technique provides a simple and convenient means of acquiring the IR spectra of a wide variety of samples; many of them are not readily convenient to IR analysis using conventional transmission measurements [34]. Some advantages of ATR are minimal or without sample preparation, fast and easy to clean up, analysis of sample in their natural states and excellent for thick or strongly absorbing samples [24]. According to our experience almost all kind of samples can be well analysed using ATR i.e. drug raw materials, drug preparations, powdered herbal drugs, dried leaves, plastics, liquids, etc.

2.2.3.3 Diffuse Reflection Infrared Fourier Transform Spectroscopy (DRIFTS)

By this method sample was mixed 90–99% with an IR diluent transparent matrix (e.g. as KBr). DRIFTS can be applied of both powdered organic and inorganic (<10 μm). The IR radiation will interact with the sample particles and then will reflect off their surfaces, causing the light to diffuse, or scatter, as it moves throughout the analysed sample. The scattered light is then directed into the detector. The advantages of this method are almost no sample preparation, no need to form KBr pellets and relatively fast [23, 24]. The original DRIFTS spectrum is recorded as diffuse reflectance (R%) vs. wave numbers, which is the ratio of single beam spectrum of the sample to that of non-absorbent references. Since R% is not linear with concentrations, generally it is converted to log (1/R) for NIR spectra, while for MIR it should be converted to Kubelka-Munk function. For sample with a higher absorption index, larger particle size and higher refractive index, interference of specular reflection becomes more significant [27].

2.2.3.4 FT-IR Microscopy

FT-IR Microscopy (FT-IR-M) comprises a FT-IR spectrometer, an infrared detector and an optical microscopy. The microscope must be free from any glass lenses, as glass can absorb all IR light. Therefore, the optical elements used are gold- or aluminium-coated mirrors, or some other windows with IR transparent [35]. The central elements of an infrared microscope are a pair of reflective condensing objectives with a Schwarzschild/Cassegrain design, which focus/collect light to/from samples, allowing both transmission and reflection spectroscopy [36]. Typically, FT-IR-M can be measured using either transmission-, or reflection-mode [37, 38]. The infrared pathway in a PerkinElmer Spotlight 200 FT-IR-M system was illustrated by Fig. 2.4 (in transmittance form) and Fig. 2.5 (in reflectance form) [39]. The quality of the FT-IR-M spectra was affected by spatial resolution, signal-to-noise ratio and the spectra artefacts, which could be defined as the variation of absorbance or location of spectral bands due to non-chemical effects [38]. Two types of MIR array detectors commercially available for FT-IR-M are linear and focal plane array (FPA). FPA detector can be used from near infrared to 900 cm^{-1}, while a 16 pixels linear array can be used for measurement to lower wavenumbers (720 cm^{-1}) [37]. New FPA detector is comprised of a matrix of 16 × 16 up to 128 × 128 detector elements; this allows user to acquire up to 16,000 pixels/spectra simultaneously [40]. The relatively new Linear Array Detector (LAD), capable of incorporating

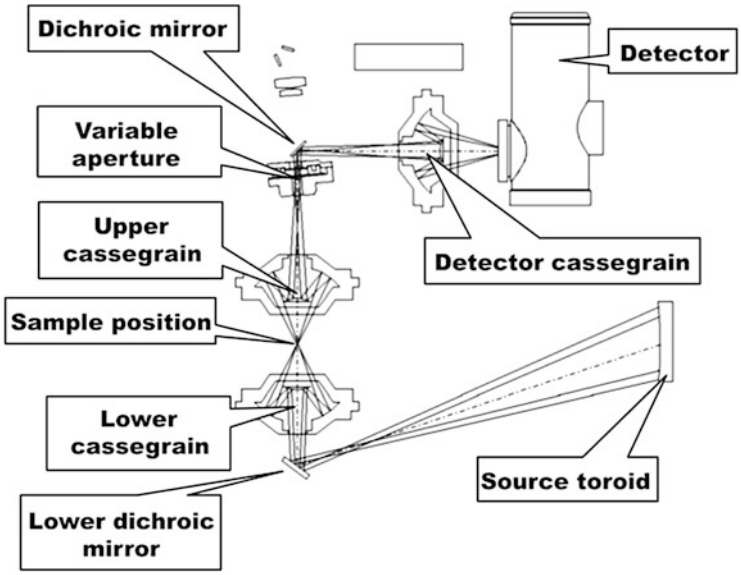

Fig. 2.4 Path of the infrared beam for collecting an image in transmittance in spotlight 200 FT-IR microscopy system. Light from the spectrophotometer is reflected off the toroid onto the lower dichroic mirror which sends it through lower Cassegrain; the upper dichroic mirror reflects the beam onto the detector Cassegrain; the detector Cassegrain focuses onto the detector (Courtesy of PerkinElmer, Shelton, CT 06484, USA) [41]

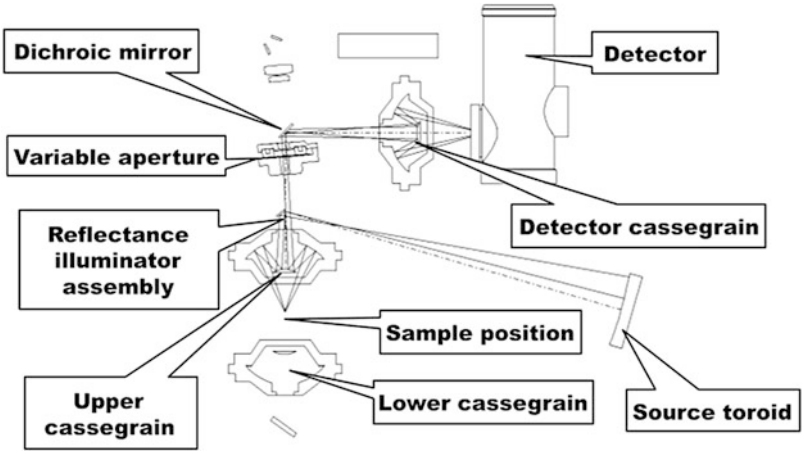

Fig. 2.5 Path of the infrared beam for collecting IR spectra in reflectance in spotlight 200 FT-IR microscopy system. The toroid moves to send the beam to the reflectance illuminator assembly dichroic mirror, which sends it to through upper Cassegrain; The beam reflected off sample and back through to the other side of Cassegrain toward the remote aperture; the detector Cassegrain focuses onto the detector (Courtesy of PerkinElmer, Shelton, CT 06484, USA) [41]

high-quality mercury cadmium telluride (MCT) is arranged as 16 gold-wired IR detector elements. MCT has been already patented by Perkin Elmer, and MCT detector can measure up to wavenumbers of 580 cm^{-1} [39]. The spatial resolution is depended to its numerical aperture (NA), while the smallest distance (δ) at which two points of the analysed sample can still be separated is inversely proportional to NA ($\delta = 0.61\ \lambda/NA$).

Because the numerical aperture of the objective mirror in FTIR microscopes is about 0.6, then δ value is equal to wavelength λ [40]. For transmission mode sample can be placed directly on sample windows that employ IR transparent materials (NaCl or BaF_2); BaF_2 is preferred due to its low water solubility. If the sample is too thick it can be flattened by using a roller blade or a micro compression cell; other method for transmittance mode is by placing the sample in two diamond windows, or as a thin section that can be obtained by microtome. ATR FT-IR-M is frequently used for reflectance mode by using a micro-ATR objective; Germanium (5500–600 cm^{-1}) and Silicon (7800–800 cm^{-1}) are generally used as ATR objective crystal materials [41–43]. Recently Agilent developed a Laser Direct Infrared Imaging System (LDIR); this LDIR can relatively collect data faster compared to conventional FT-IR-M [44]. The main advantage of applying FT-IR-M is non-invasive; it does not need staining or labelling of the sample; the molecules are identified based on their characteristic IR vibrations. FT-IR-M delivers the group of compound information of the targeted area. Therefore FT-IR-M is also called as *chemical imaging* method [40].

2.2.3.5 Two-Dimension FT-IR Correlation Spectroscopy (2D FT-IR)

Sometimes it is very difficult to differentiate different samples by carrying out a conventional FT-IR only (absorbance- or transmission-mode) due to their close similarity. To overcome this problem, the conventional FT-IR spectra can be converted to their second derivative infrared spectra, and/or performing a 2D FT-IR [26]. 2D FT-IR can be prepared by using a KBr pellet, which will be perturbed by some physical or chemical stimulus using a special device; these stimuli will induce a dynamic 2D spectrum. A physical thermal stimulus was usually used for preparing a 2D FT-IR spectrum [45]. As example, 2D FT-IR spectra of some *Polygonum minus* can be prepared by using a thermal stimulus at certain range of temperatures (e.g. 40–120 °C, interval of 10 °C) [46]. The dynamic 2D infrared spectra can be obtained by plotting absorbance intensities and variables (wave number and perturbations); the spectra can be shown as three-dimensional spectra or as a contour plot. Two-dimension (2D) correlation infrared spectra, synchronous and asynchronous 2D, can be directly observed. A synchronous 2D FT-IR spectra of powdered *Curcuma longa* (KBr pellet) which was prepared at our laboratory was presented in Fig. 2.6 (unpublished work).

In synchronous FTIR spectrum, peaks presented the coincidence of the spectral intensity's differences (increase or decrease) at corresponding variables wave numbers v_i and v_j during perturbations. The synchronous correlation intensity of wave numbers (v_i, v_j) characterizes the degree of coherence between two signals that are measured concurrently. This intensity becomes maximum if the variations

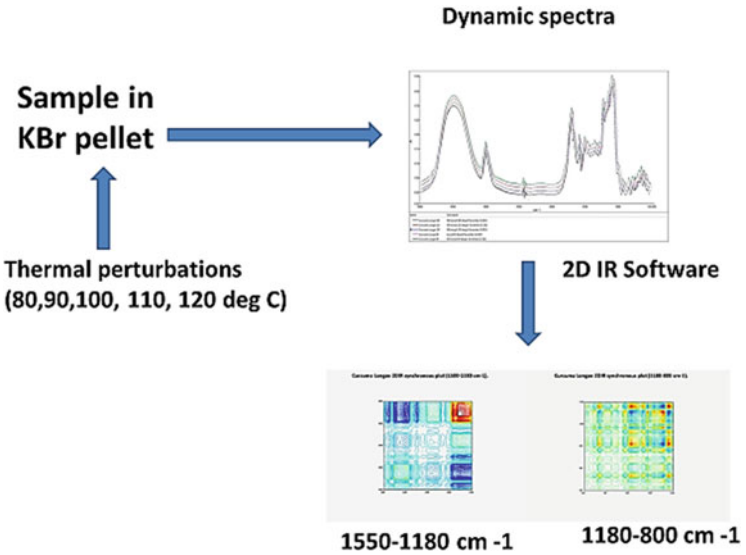

Fig. 2.6 How to generate two-dimension (2D) correlation spectrum of powdered *Curcuma longa* by using five levels thermal perturbations (unpublished results)

of the two dynamic IR signals are totally in phase with each other, and minimum if they are antiphase. IR signals which are nearly orthogonal to each other should yield almost no synchronous correlation intensity. A cross peak (at v_i, v_j) was observed if the spectral intensities at v_i and v_j changed instantaneously when perturbation was applied. The cross peak is positive if the intensities of v_i and v_j both increase (or decrease) along the perturbation, otherwise the cross peak is negative. 2D FT-IR spectrum is symmetric with respect to the diagonal line in the synchronous spectra. The variation of the spectra intensity at a variable is always the same as itself so there are only positive peaks that defined as auto peaks along the diagonal of the 2D synchronous spectrum. An auto peak characterizes the overall susceptibility of the spectral signal to change intensity when an external perturbation is applied [26, 45].

The asynchronous spectra afford the sequence of the spectral intensities' variations at different wave numbers v_i and v_j during the perturbations. The asynchronous correlation intensity on the other hand will characterize the coherence degree between signals measured at two different instances, which are separated by a correlation time. The asynchronous correlation intensity will be maximum if the dynamic signals are orthogonal to each other, and will be minimum when the signals are exactly in phase or antiphase with each other. A cross peak at v_i, v_j is detected if the spectral intensities at v_i changed before or after the variations of v_j. No diagonal peaks are observed in asynchronous 2D correlation spectrum [26, 45].

2.3 Chemometrics

The success of FTIR spectroscopy for analysis of food composition is supported by statistical analysis and chemometrics. Fortunately, some sophisticated instruments were equipped with statistical and chemometrics software [47]. Chemometrics, also known as multivariate data analysis (MDA), is a branch of chemistry which apply mathematics and statistics sciences to treat chemical data either qualitative or quantitative data (pH, concentrations, weights, etc.). Some topics are covered in chemometrics, namely descriptive statistics, the experimental design, process optimization, signal detection and signal processing, multivariate calibration, classification modelling and analytical quality assurance [48]. Chemical data typically include properties and values of numerous compounds as determined by instrumental methods and having various sources of variance. Accordingly, statistical evaluation of such data should use one or more multivariate data statistics (chemometrics). Multivariate statistics allows the simultaneous analysis of several independent variables (factors) against several dependent variables or responses [49].

Chemometrics is exploited for multivariate data collection and analysis protocols, calibration modelling, classification and cluster modelling, signal correction and compression, method optimization and statistical process control. Singh et al. [50] stated that chemometrics is useful means for the real-time in-process testing and is a valuable process analytical tool. In general, chemometrics or MDA are categorized in two classes: (a) chemometrics for qualitative data analysis intended for identification or classification purposes using pattern recognition methods and (b) multivariate calibration intended for facilitating the quantitative analytical purposes.

In analytical purposes, the most widely uses of MVA in FTIR spectra include confirmation, qualitative analysis, purity test and quantitative analysis of food components are (a) FTIR spectra processing by applying some pre-treatment spectra of mean centring, Savitzky-Golay derivatization, smoothing, etc. Spectra pre-treatment can enhance the accuracy and robustness of spectra resulting in reliable data, while spectra derivatization (1st, 2nd, 3th or higher order) can enhance the resolution of overlapping peaks [51–53]; (b) pattern recognition either unsupervised such as principal component analysis and cluster analysis or supervised like discriminant analysis with its algorithm variations; (c) multivariate calibrations (MC) using several algorithms including principle component regression and partial least square; (d) experimental design typically used for optimization of analytical conditions during food analysis [55]. Some methods such as analysis of variance and response surface methodology are widely used for optimization of factors affecting food analysis [54].

The steps of analytical procedures which involved FTIR spectroscopy and chemometrics techniques in food analysis can be briefly described as: (a) definition of food analysis problems, i.e. confirmation, identification (qualitative analysis) or quantitative analysis, (b) sampling process, (c) acquisition of FTIR spectra using

FTIR spectrophotometer, (d) pre-treatment (processing) of FTIR spectral data, (e) selection of chemometrics models, (f) selecting calibration and validation sets of samples, (g) the chemometrics model optimization in calibration using selected variables, namely absorbance values at specific wavenumbers region, (h) validation of chemometrics model and (i) making conclusion of chemometrics models [56]. All these steps can be assisted using sophisticated statistics software, among these are Minitab®, Unscrambler®, SIMCA® SIRIUS®, Matlab® and Pirouette®, Grams® 32 [57, 58]. Currently, free interface software of Chemoface has been developed by Prof. Cleiton A. Nunes et al. for chemometrics analysis [59].

2.4 Applications of FT-IR for Food Analysis

Some books and review articles, which described and discussed the general application of FT-IR for the analysis and quality control of food preparations, have been published in the last ten years. In 2009, Sun [27] edited a book entitled "Infrared Spectroscopy for Food Quality Analysis and Control", this book consisted of seven chapters on fundamental/instrumentation, and eight chapters for applications, which were comprised of meat, fish, milk, cereal, fruit and vegetable, fruit juice, wine and beer, egg and related products. Sun et al. [26] published a nice book that discussed in detail the methods and application of FT-IR for the analysis of complex mixtures of foods and traditional Chinese medicines. Rodriguez-Saona and Allendorf [60] wrote a review article on the application of FT-IR combined with MVA for the authentication and detection of food's adulterants. A mini review on the application of mid-infrared as a tool for phenotyping tool of milk trait has been published by Marchi et al. [61]. Khan et al. [62] described the application of FT-IR for identification of food's adulterants in honey, milk, wines, fat and oils. A review article on the application of FT-IR for detecting specific regulated or toxic plant in plant food supplements and herbal drugs has been published by Deconinck et al. [63]. Su and Sun [64] published a review article on the application of FT-IR, Raman and hyperspectral imaging techniques for quality determinations of powdery foods (e.g. milk, tea, cocoa, coffee, soybean floor, wheat flour, culinary powder). Application of FT-IR for checking the quality and safety of fat and oils was recently reviewed by Li et al. [65]. FTIR and its combination with various techniques (NIR, MS) for detecting food adulterants has been reviewed by Valand et al. [66]. Furthermore, Rohman [5] published mini review on the application of FT-IR for traceability and authentication of meat and meat products.

The objectives of the applications of FT-IR, 2D FT-IR combined with multivariate analysis (MVA) or chemometrics for analysis of food, which were described and discussed in books and article, which were cited in this present chapter, can be been summarized in Box 2.1. Our experiences showed that all kind of raw material (RM) from plant origin (including leaves, fruits, beans, herbs, etc.), meats and related animal products can be analysed by FT-IR. Sun et al. [67] and Sun et al. [26] have outlined *a tri-level infrared identification* for qualitative analysis by using FT-IR. Sample usually could be identified or differentiated by comparing

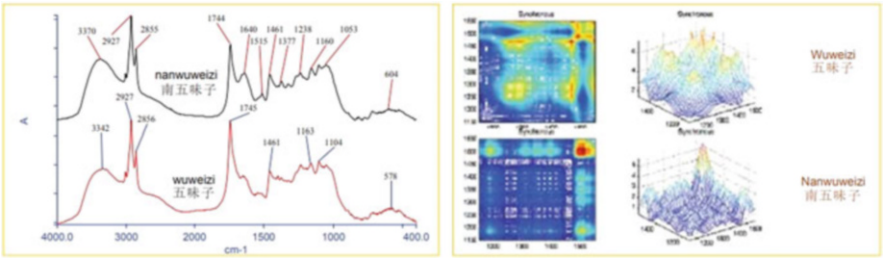

Fig. 2.7 By using two-dimension Fourier transform infrared (2D FT-IR) sample of Wuweizi (*Schisandrae chinensis* Fructus) and Nanwuweizi (*Schisandrae sphenantherae* Fructus) (Courtesy of PerkinElmer, Shelton, CT 06484, USA) [39]

their FT-IR spectra, and this is known as primary identification. The secondary step of identification is based on the second derivative infrared spectroscopy (SD-IR); some overlapped peaks, which were observed in the primary identification could be well differentiated by using SD-IR. In case, it was not possible for identification of a sample by using primary- and secondary-step, due to almost similar observed spectra, a two-dimensional correlation infrared (2D-IR) spectroscopy method can be applied; this 2D-IR is known as a tertiary step of identification method. Figure 2.7 showed the FT-IR spectra of the two fruits, which were similar, so the differentiation of those two fruits was difficult, but by using 2D FT-IR, both fruits can be easily discriminated. For identification and classification purposes by using primary and secondary identification methods, generally MVA was applied for data evaluations (e.g. PCA, PLS-DA, SIMCA). See Sect. 2.3.

Quantitative analysis by FT-IR can be performed by construction of a linear regression between concentrations of standard against the ratio of intensities of two specific wave number of the absorption FT-IR spectra; concentration of sample can be calculated from the linear calibration regression curve [26]. Quantitative analysis of the sample can be also done also using MVA (PLS); this will be discussed in section Chemometrics. It is very important to note, that before any data collections, method validation should be first performed. This present review will be focused on the application of FT-IR for analysing for fat, oil, fruits, beans and related products which appeared in the last ten years.

2.4.1 Application of FT-IR for Fruits, Beans and Related Products

The objective of application of FTIR spectroscopy in combination with multivariate data analysis (MVA) in food analysis is compiled in Box 2.1. Furthermore, Table 2.1 summarized publications that reported the application of FT-IR for analysing fruits, beans and related products. As shown in the table, ATR method was the most used method, this could be due to its simplicity of the method. Almost all publication used MVA for evaluations the FT-IR data.

Table 2.1 Application of FT-IR for analysing fruit, beans, nectar and its related preparations

Material	IR method	Sample for analysis	Measured/specific bands (cm^{-1})	Chemometrics[a]	Objective	Ref. (application[b])
Nectars	ATR	Nectars transferred to ATR surface	1200–900	PLS, OPS, GA	Quantification of a certain nectars in original- and adulterant-sample	[71] (b, h)
Fruits, vegetables	ATR	100 mesh powdered raw material (RM) and alcohol insoluble solids (ASI) transferred to ATR surface	1740 (neutral sugars); 1075, 1440–1450, 1616 and 1740 (pectin); 895, 1035–1041 and 1160–1163 (cellulose); 1035–1041 (lignin)	ANOVA, PCA, PLS	Determination of cell wall composition based on certain group of compounds	[72] (f)
Citrus fruits	ATR	Supernatant of MeOH extracts was dispensed into a 384-well zinc selenide (ZnSe) plate, and dried at 37 °C	1800–800	PCA, PLS-DA, PLS	Determination of total carotenoids, flavonoids and phenolic compounds in fruits	[73] (f)
Citrus fruits	ATR	Supernatant of MeOH extracts was dispensed into a 384-well zinc selenide (ZnSe) plate, and dried at 37 °C	950–1100, 1300–1500, and 1500–1700	PCA, PLS-DA, HCA	Discrimination of Citrus lines, and prediction sugar and acid content in fruits	[74] (a, f)
Drink fruit juices	ATR	Water solutions of sugars and Juices	900–1400	PCA, PLS	Prediction of sugars and acid contents	[74] (f)
Pineapple (*Ananas comosus* L.) by-products (core and shell)	ATR	Lyophilized pineapple by-product	4000–600	PCA, PLS	Determination of phenolic content and antioxidants in treatment's pineapple	[75] (a, f)
Mangoes fruit	DRIFFT	Approximately 2 mg of homogenized freeze-dried mango pulps were transferred to the DRIFT sample holder cup	1500–750	PCA, PLS	Determination of glucose and sucrose	[76] (f)

Tomato fruit	ATR	Whole tomato fruit was placed on the sample stage for analysis, with no more than 0.1 kg of applied pressure	1800–900	PCA-LDA	Determination of ripening processes of the tomato	[77] (a)
Mango fruit	DRIFFT	2 mg of freeze-dried mango samples transferred to the DRIFT sample holder cup	1250–740, 780 (7-cis β-carotene); 2922, 2862 (α-tocopherol); 2933, 2940 (ascorbic acid)	Random Forest of 1st derivative spectra and ANOVA	Determination of β-carotene, α-tocopherol and l-ascorbic acid	[78] (f)
Red plum-, persimmon-, peach- and kiwi-fruits	ATR	Fruit extract (extractor: 50% methanol/water, or 1.2 mol/L HCl in 50 mL/100 mL methanol/water then heating at 90 °C for 3 h)	1800–600	NA	Qualitative identification of poly phenols. Using catechin as standard	[79] (f)
Grape, carob and mulberry *Pekmez* (juices)	ATR	Adulterated and pure grape, carob and mulberry pekmez samples	1500–800	PLS, PLS-DA	Discriminate original and adulterant's juices	[80] (b)
Coffee samples	Transmission, DRIFFT, ATR	Ground coffee (GC) and KBr (1/50) for pellet (transmission); 1 mg GC mixed with 150 mg KBr (Driff)	3200–700	PCA, HCA	Discrimination of defective and non-defective coffee samples	[81] (c)
Green coffee bean samples	ATR	Liquid-nitrogen frozen green coffee beans were finely ground using a mortar	4000–600, (2750–1775) was removed before evaluations	PCA, PLS	Distinguishing green coffee beans from different origins	[82] (a)
Ayocote bean starches	Transmission	Powered samples mixed with dry KBr	4000–500	NA	Studying the effect of thermal and extraction on the characteristic of bean starches	[83] (a, g)

(continued)

Table 2.1 (continued)

Material	IR method	Sample for analysis	Measured/specific bands (cm^{-1})	Chemometrics[a]	Objective	Ref. (application[b])
Nespresso® coffee pods and Americano coffee pods	ATR	Approximately (1 g) of the roasted and ground coffee was placed in the sampling accessory	1800–1550	PCA, HCA	Differentiating Espresso and Americano coffee pods	[84] (d)
Powdered rice beans 40 mesh	Transmission	Powdered rice beans mixed with KBr	4000–500	NA	Studying the effect of thermal and extraction on the characteristic of rice starches	[85] (a)
Beans	ATR, 2D	Placing the samples directly onto the attenuated total reflection (ATR) crystal	3700–700 4000–1000 (for 2D)	PLS, PLSR	Determination of protein, starch and total amylose in common beans correlation between MIR and NIR	[86] (f)
Honey samples	ATR	Samples were placed on diamond/ZnSe crystal plate	1800–750	PCA, HCA	Determination of honey floral source	[87] (a)
Flour of some wheat grains	NA	Flour of each wheat variety was collected. These flour samples were converted into pellets and pellets were cut into thin sections. These thin sections were oven dried and their spectra were recorded on FTIR	1640–3300 (moisture); 1600–1700, 1550–1570 (crude fat); 1600–1700, 1550–1570 (crude protein); 800–1500, 2800–3000, 3000–3600 (starch)	NA	Qualitative identification of wheat varieties	[88] (a)

Strawberry fruits	Transmission using gaseous cell, 2D FT-IR	Using special device gas sampling	4000–600	PCA, 2D software	Determination spoilage process of strawberries	[89] (a)
Fruits peel	Transmission	Special gas sampling system designed by the authors	2990–2830 and 1259–1227	PCA	Detection of pesticide (chlorpyrifos) residues on fruit peels	[90] (f)
Cocoa beans and chocolate produced	ATR	Freeze-dried chocolate and cocoa beans were transferred onto ATR crystal	4400–600	PCA, PLS, PLSR	Prediction of the total phenol content and total antioxidant	[91] (f)
Crude coffee oil	ATR	An aliquot of 1 ml of the oil sample in a thin film was used for FTIR	3050–2800 (hydrogen's stretching vibrations); 1780–1680 (carbonyl stretching vibrations)	ANOVA	Differentiating roasted coffee oil and heated roasted coffee oil	[92] (a, e)
Soybeans	ATR	Soybean powder was loaded onto ATR crystal	4000–400	PLS-DA, PLSR	Discrimination and prediction of the origin of Chinese and Korean soybeans	[93] (a)

[a] *PLS* partial least square, *OPS* ordered predictor selection, *GA* genetic algorithm, *ANOVA* analysis of variance, *PCA* principal component analysis, *PLS-DA* partial least square-discriminant analysis, *HCA* hierarchal cluster analysis, *PLSR* partial least square regression, *NA* not available

[b] See Box 2.1

Box 2.1 The Objectives of the Application of Combination FT-IR, 2D FT-IR and MVA for Food Analysis[a]

a. Identification of raw RM; discrimination of the same RM, which was based on variants, geographical origins, harvested time and treatments
b. Rapid identification of genuine and counterfeit products
c. Quality control of the products
d. Differentiate products from different manufacturers
e. Stability evaluation of the RM and related products
f. Performing qualitative and quantitative analysis of compounds or group of compounds in RM and/or products
g. Monitoring and analysing the manufacturing and extraction processes
h. Performing rapid qualitative identification of RM in various formulations of the product.

[a]Modified from PerkinElmer, Complete Solution for Traditional Medicine Research and Analysis [68]

The distribution of certain class compounds (e.g. lipids and or sugars) in the cross section of a tomato fruit can be clearly observed by using FT-IR-M. Figure 2.8 showed the distribution of the absorbance at 1740 cm^{-1} (C=O lipid) corresponding to the lipid distribution, while Fig. 2.9 showed the distribution of sugars or carbohydrate can be detected using absorbance at 1050 cm^{-1} (OH); the red area corresponds to a high concentration of lipid relative to the blue area. The distributions and relative concentrations of proteins, carbohydrates and the waxes/lipids in the cross section of a wheat stem can be also easily determined by using FT-IR-M [40]. This showed that FT-IR Microscopy can be well used for searching and determining the locations and distribution of a certain compound or group of compounds in certain tissue(s) or organ(s) of plant and animal. Unfortunately, there is not many works that have been published on the application of FT-IR-M for food analysis.

2.5 Advantages and Disadvantages of Infrared Spectroscopy in Food Analysis

Some advantages of the application of FT-IR in food analysis are: the FT-IR spectrometer is relative cheap, sample preparation is simple, sample also can direct to be measured without any sample preparation, a small of amount of sample is required, non-destructive method of analysis, less use of hazardous solvent and decreasing hazard to environmental and human, rapid detection, analysing time is relatively very fast, various sample analysis can be analysis (such as, solids, liquids, semi-solids, powder samples, herbs etc.), relatively low operational cost, FT-IR can be used for both quantitative and qualitative methods, repeatability of the measurements is relative good, by using standardized method good reproducibility

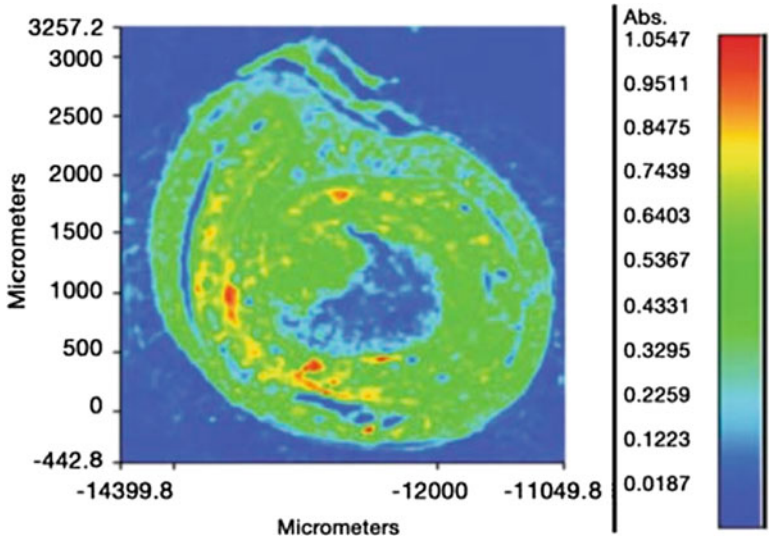

Fig. 2.8 Distribution of the absorbance at 1740 cm^{-1} corresponding to the lipid's distribution in the cross section of tomato (Courtesy of PerkinElmer, Shelton, CT 06484, USA) [39]

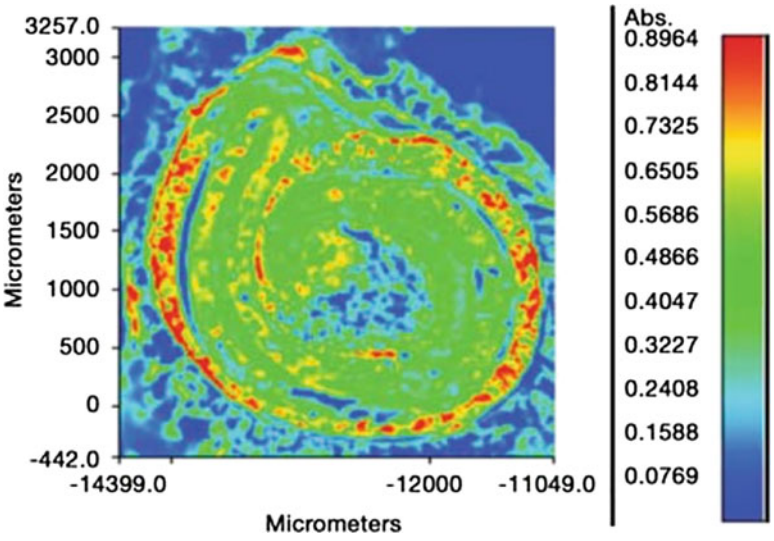

Fig. 2.9 Distribution of the absorbance at 1050 cm^{-1} corresponding to the sugar's distribution in the cross section of tomato (Courtesy of PerkinElmer, Shelton, CT 06484, USA) [39]

can be achieved. The disadvantages of FT-IR are: biological samples are difficult to analyse using FT-IR due to strong absorption of OH, FT-IR is sensitive to the environment change (CO_2 and water vapour can affect the spectra), FT-IR cannot detect atoms and monoatomic ions, elements or inert gas, FT-IR cannot detect

diatomic molecules such as nitrogen and oxygen [67, 69]. To overcome the problem of analysing biological fluids by FT-IR, Pupeza et al. [70] proposed a new method called Field-resolved infrared spectroscopy; detailed discussion of the new method can be referred in their recent publication.

2.6 Conclusion

Infrared spectroscopy method equipped with modern instrument and sampling handling technique such as attenuated total reflectance, Diffuse reflection infrared Fourier transform spectroscopy (DRIFTS), FTIR microscopy and Two-Dimension FT-IR Correlation Spectroscopy (2D FT-IR) is ideal technique for qualitative and quantitative analyses of food composition due to its capability to provide fingerprinting technique. FTIR spectroscopy is widely used for food composition analysis intended to confirmation and identification of raw materials, discrimination of food from different origin, authentication of food products as well as the monitoring and quality control of food production. In the future, the miniature of FTIR spectroscopy instrumentation makes this technique suitable for on-site application for rapid quality control.

Acknowledgements The authors are thankful to Dr. Teo Wei Boon (PerkinElmer, Singapore) for preparing 2D-FT-IR of *Curcuma longa* during short visit at the Faculty of Pharmacy, Airlangga University, Surabaya (2016), Dr. Robert Packer (PerkinElmer, Shelton, CA, USA) and Dr. Tan Boon Chun (PerkinElmer Selangor, Malaysia) for permission to reproduce some figures, Ms. Febry Ardiana (PT Bernofarm, Sidoarjo, Surabaya) for reference (USP 42, General method <854>) [23].

References

1. Pavia DL, Lampman GM, Kriz GS (2001) Introduction to spectroscopy, 3rd edn. Thomson Learning, Inc., Boston, p 579
2. Cozzolino D (2014) An overview of the use of infrared spectroscopy and chemometrics in authenticity and traceability of cereals. Food Res Int 60:262–265. https://doi.org/10.1016/j.foodres.2013.08.034
3. Teixeira AM, Sousa C (2019) A review on the application of vibrational spectroscopy to the chemistry of nuts. Food Chem 277:713–724. https://doi.org/10.1016/j.foodchem.2018.11.030
4. Tan HP, Ling SK, Chuah CH (2011) One- and two-dimensional Fourier transform infrared correlation spectroscopy of Phyllagathis rotundifolia. J Mol Struct 1006(1–3):297–302. https://doi.org/10.1016/j.molstruc.2011.09.023
5. Rohman A (2019) The employment of Fourier transform infrared spectroscopy coupled with chemometrics techniques for traceability and authentication of meat and meat products. J Adv Vet Anim Res 6(1):9–17
6. Moros J, Garrigues S, De Guardia M (2010) Vibrational spectroscopy provides a green tool for multi-component analysis. Trends Anal Chem 29(7):578–591. https://doi.org/10.1016/j.trac.2009.12.012
7. Gredilla A, De Vallejuelo SF, Elejoste N, De Diego A, Madariaga JM (2016) Trends in analytical chemistry non-destructive spectroscopy combined with chemometrics as a tool for green chemical analysis of environmental samples: a review. Trends Anal Chem 76:30–39. https://doi.org/10.1016/j.trac.2015.11.011

8. Li YS, Church JS (2014) Raman spectroscopy in the analysis of food and pharmaceutical nanomaterials. J Food Drug Anal 22(1):29–48. https://doi.org/10.1016/j.jfda.2014.01.003
9. Callao MP, Ruisánchez I (2018) An overview of multivariate qualitative methods for food fraud detection. Food Control 86:283–293
10. Pallone JAL, dos Caramês ET, Alamar PD (2018) Green analytical chemistry applied in food analysis: alternative techniques. Curr Opin Food Sci 22:115–121
11. Maree JE, Viljoen AM (2011) Fourier transform near- and mid-infrared spectroscopy can distinguish between the commercially important Pelargonium sidoides and its close taxonomic ally P. reniforme. Vib Spectrosc 55(2):146–152. https://doi.org/10.1016/j.vibspec.2010.10.005
12. Man YBC, Syahariza ZA, Rohman A (2011) Fourier transform infrared (FTIR) spectroscopy: development, techniques, and application in the analyses of fats and oils. In: Fourier transform infrared spectroscopy: developments, techniques and applications. Nova Science Publisher, New York
13. Chakraborty DS (2016) Instrumentation of FTIR and its herbal applications. World J Pharm Pharm Sci 5(3):498–505
14. Rohman A (2017) The use of infrared spectroscopy in combination with chemometrics for quality control and authentication of edible fats and oils: A review. Appl Spectrosc Rev 52:7
15. Ma G, Allen HC (2004) Handbook of Spectroscopy, Volumes 1 and 2 Edited by Günter Gauglitz (University of Tübingen) and Tuan Vo-Dinh (Oak Ridge National Laboratory). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2003. 1168 pp. $435.00. ISBN: 3-527-29782-0. Vol. 126. J Am Chem Soc 34:8859–8860
16. Ballabio D, Todeschini R (2009) Infrared spectroscopy for food quality analysis and control multivariate classification for qualitative analysis. Infrared Spectrosc Food Qual Anal Control 2009:83–104
17. von Aulock FW, Kennedy BM, Schipper CI, Castro JM, Martin D, Oze C et al (2014) Advances in Fourier transform infrared spectroscopy of natural glasses: From sample preparation to data analysis. Lithos 206–207(1):52–64. https://doi.org/10.1016/j.lithos.2014.07.017
18. Hashimoto K, Badarla VR, Kawai A, Ideguchi T (2019) Complementary vibrational spectroscopy. Nat Commun 10(1):1–6. https://doi.org/10.1038/s41467-019-12442-9
19. Davis SP, Abrams MC, Brault JW (2001) Theory of the ideal instrument. Fourier Transform Spectrom 2001:29–39
20. Robertson M, Elements V, Table P, Library B, Society TR, Society TR et al (2004) Organic spectroscopic analysis
21. Baeten V, Dardenne P (2002) Spectroscopy: Developments in instrumentation and analysis. Grasas Aceites 53(1):45–63
22. Stuart BH (2004) Infrared spectroscopy: fundamentals and applications, vol. 8, Methods, p 224. Available from http://doi.wiley.com/10.1002/0470011149
23. United Stated Pharmacopeia (USP) 42, General method <854> mid infrared spectroscopy. https://online.uspnf.com/uspnf/document/GUID-21493947-8F57-4FC7-9338-FD47C1354A3A_4_en-US?highlight=854 © 2019 USPC. November 15, 2019
24. Thermo Scientific (2013) Introduction to FT-IR sample handling. Thermo Fish Sci Inc., Waltham, pp 1–8
25. Shimadzu. Measurement Methods for Powder Samples : SHIMADZU (Shimadzu Corporation). [cited 2020 Mar 21]. Available from https://www.shimadzu.com/an/ftir/support/ftirtalk/talk8/intro.html
26. Sun S-Q, Zhou Q, Chen J-B (2020) Infrared spectroscopy for complex mixtures: applications in food and traditional Chinese medicine. 2011 [cited 2020 Mar 21]. Available from http://books.google.es/books/about/Infrared_Spectroscopy_for_Complex_Mixtur.html?id=SUhIMwEACAAJ&pgis=1
27. Sun DW (2009) Infrared spectroscopy for food quality analysis and control. infrared spectroscopy for food quality analysis and control. Elsevier Inc., Amsterdam
28. Thermo Scientific (2019) Move from investigate to solve Forensics compendium. Move from investigate to solve Forensics compendium. Thermo Scientific, Waltham

29. PerkinElmer (2005) FT-IR Spectroscopy Attenuated Total Reflectance (ATR). PerkinElmer Life Anal Sci. pp 1–5. Available from http://www.utsc.utoronto.ca/~traceslab/ATR_FTIR.pdf
30. Griffiths PR, De Haseth JA (2006) Fourier transform infrared spectrometry, 2nd edn. Wiley, Hoboken, pp 1–529
31. Sciences N, Mada UG, Utara S, Mada UG, Utara S (2017) Attenuated total reflectance-FTIR spectra combined with multivariate calibration and discrimination analysis for analysis of patchouli oil adulteration. Indones J Chem 1:1–8
32. Smith BC (2002) Quantitative spectroscopy: theory and practice. Elsevier, Amsterdam, p 212
33. Bruker Optics Inc. Attenuated Total Reflection (ATR) – a versatile tool for FT-IR spectroscopy. Appl Note AN # 79. 2011. p 4
34. Van De Voort FR, Sedman J, Russin T (2001) Lipid analysis by vibrational spectroscopy. Eur J Lipid Sci Technol 103(12):815–826
35. Wellner N (2013) Fourier transform infrared (FTIR) and Raman microscopy: principles and applications to food microstructures. In: Food microstructures: microscopy, measurement and modelling. Elsevier Ltd, Amsterdam, pp 163–191
36. Infrared Microscopy Applications. [cited 2020 Mar 21]. Available from https://www.gia.edu/gia-news-research-Infrared-Microscopy-Applications
37. Kazarian SG, KLA C (2013) ATR-FTIR spectroscopic imaging: recent advances and applications to biological systems, vol 138. Royal Society of Chemistry, London, pp 1940–1951
38. Kimber JA, Kazarian SG (2017) Spectroscopic imaging of biomaterials and biological systems with FTIR microscopy or with quantum cascade lasers. Anal Bioanal Chem 409(25):5813–5820
39. Perkinelmer. Infrared Imaging and Microscopy Systems. [cited 2020 Mar 21]. Available from: https://www.perkinelmer.com/lab-solutions/resources/docs/BRO_Spotlight400A.pdf
40. Bruker Optics Inc. FT-IR microscopy - a powerful chemical imaging tool. [cited 2020 Mar 21]. Available from https://www.azom.com/article.aspx?ArticleID=5949
41. PerkinElmer, Inc. Spotlight 200 FT-IR microscopy system redefining IR microscopy. [cited 2020 Mar 21]. Available from www.perkinelmer.com
42. Maryse JEM. Application of FTIR microscopy to cultural heritage materials . 2009. [cited 2020 Mar 21]. Available from: http://amsdottorato.unibo.it/1404/
43. Prati S, Joseph E, Sciutto G, Mazzeo R (2010) New advances in the application of FTIR microscopy and spectroscopy for the characterization of artistic materials. Acc Chem Res 43(6):792–801
44. Paper W. Microplastics analysis doesn't need to be so hard simplify microplastics analysis through a rapid
45. Noda I (1990) Two-dimensional infrared (2D IR) spectroscopy: theory and applications. Appl Spectrosc 44(4):550–561
46. Khairudin K, Sukiran NA, Goh HH, Baharum SN, Noor NM (2014) Direct discrimination of different plant populations and study on temperature effects by Fourier transform infrared spectroscopy. Metabolomics 10(2):203–211
47. Rohman A, Arsanti L, Erwanto Y, Pranoto Y (2016) The use of vibrational spectroscopy and chemometrics in the analysis of pig derivatives for halal authentication. Int Food Res J 23:5
48. Daszykowski M, Walczak B (2006) Use and abuse of chemometrics in chromatography. TrAC - Trends Anal Chem 25(11):1081–1096
49. Granato D, Putnik P, Kovačević DB, Santos JS, Calado V, Rocha RS et al (2018) Trends in chemometrics: food authentication, microbiology, and effects of processing. Compr Rev Food Sci Food Saf 17(3):663–677
50. Singh SK, Jha SK, Chaudhary A, Yadava RDS, Rai SB (2010) Quality control of herbal medicines by using spectroscopic techniques and multivariate statistical analysis. Pharm Biol 48(2):134–141
51. Ferreira GWD, Roque JV, Soares EMB, Silva IR, Silva EF, Vasconcelos A et al (2018) Temporal decomposition sampling and chemical characterization of eucalyptus harvest residues using NIR spectroscopy and chemometric methods. Talanta 188:168–177

52. Lasch P (2012) Spectral pre-processing for biomedical vibrational spectroscopy and microspectroscopic imaging. Chemom Intell Lab Syst 117:100–114
53. Lai Y, Ni Y, Kokot S (2011) Discrimination of Rhizoma Corydalis from two sources by near-infrared spectroscopy supported by the wavelet transform and least-squares support vector machine methods. Vib Spectrosc 56(2):154–160. https://doi.org/10.1016/j.vibspec.2011.01.007
54. Singh I, Juneja P, Kaur B, Kumar P (2013) Pharmaceutical Applications of Chemometric Techniques. ISRN Anal Chem 2013:1–13
55. Leardi R (2009) Experimental design in chemistry: a tutorial. Anal Chim Acta 652(1–2):161–172
56. Krakowska B, Custers D, Deconinck E, Daszykowski M (2016) Journal of Pharmaceutical and Biomedical Analysis Chemometrics and the identification of counterfeit medicines — a review. J Pharm Biomed Anal 127:112–122. https://doi.org/10.1016/j.jpba.2016.04.016
57. Gad HA, El-Ahmady SH, Abou-Shoer MI, Al-Azizi MM (2013) Application of chemometrics in authentication of herbal medicines: a review. Phytochem Anal 24(1):1–24
58. Rodionova OY, Pomerantsev AL (2006) Chemometrics: achievements and prospects. Russ Chem Rev 75(4):271–287
59. Nunes CA, Freitas MP, Pinheiro ACM, Bastos SC (2012) Chemoface: a novel free user-friendly interface for chemometrics. J Braz Chem Soc 23(11):2003–2010
60. Rodriguez-Saona LE, Allendorf ME (2011) Use of FTIR for rapid authentication and detection of adulteration of food. Annu Rev Food Sci Technol 2(1):467–483
61. De Marchi M, Toffanin V, Cassandro M, Penasa M (2014) Invited review: mid-infrared spectroscopy as phenotyping tool for milk traits. J Dairy Sci 1:1171–1186
62. Khan U, Afzaal M, Arshad MS, Imran M (2018) Non-destructive analysis of food adulteration and legitimacy by FTIR technology. J Food Ind Microbiol 1(1):1–7
63. Deconinck E, Djiogo CAS, Bothy JL, Courselle P (2017) Detection of regulated herbs and plants in plant food supplements and traditional medicines using infrared spectroscopy. J Pharm Biomed Anal 142:210–217
64. Su W-H, Sun D-W (2018) Fourier transform infrared and Raman and hyperspectral imaging techniques for quality determinations of powdery foods: a review. Compr Rev Food Sci Food Saf 17(1):104–122
65. Li Q, Chen J, Huyan Z, Kou Y, Xu L, Yu X et al (2019) Application of Fourier transform infrared spectroscopy for the quality and safety analysis of fats and oils: a review. Rev Food Science Nutr 59:3597–3611
66. Valand R, Tanna S, Lawson G, Bengtström L (2020) A review of Fourier transform infrared (FTIR) spectroscopy used in food adulteration and authenticity investigations. Food Addit Contam 37:19–38
67. Sun S, Chen J, Zhou Q, Lu G, Chan K (2010) Application of mid-infrared spectroscopy in the quality control of traditional Chinese medicines. Planta Med 76:1987–1996
68. McGraw B (2015) Reversing the traditional drug development model. PerkinElmer, Waltham, pp 1–4
69. Cheng N (2013) Application of Fourier-transform infrared (FTIR) for quality control of Swiss cheese. Ohio State Univ 84:487–492
70. Pupeza I, Huber M, Trubetskov M, Schweinberger W, Hussain SA, Hofer C et al (2020) Field-resolved infrared spectroscopy of biological systems. Nature 577(7788):52–59
71. Miaw CSW, Assis C, Silva ARCS, Cunha ML, Sena MM, de Souza SVC (2018) Determination of main fruits in adulterated nectars by ATR-FTIR spectroscopy combined with multivariate calibration and variable selection methods. Food Chem 254:272–280
72. Canteri MHG, Renard CMGC, Le Bourvellec C, Bureau S (2019) ATR-FTIR spectroscopy to determine cell wall composition: application on a large diversity of fruits and vegetables. Carbohydr Polym 212:186–196
73. Song SY, Kim CH, Im SJ, Kim IJ (2018) Discrimination of citrus fruits using FT-IR fingerprinting by quantitative prediction of bioactive compounds. Food Sci Biotechnol 27(2):367–374

74. Song SY, Lee YK, Kim IJ (2016) Sugar and acid content of citrus prediction modeling using FT-IR fingerprinting in combination with multivariate statistical analysis. Food Chem 190:1027–1032
75. Santos DI, Neiva Correia MJ, Mateus MM, Saraiva JA, Vicente AA, Moldão M (2019) Fourier transform infrared (FT-IR) spectroscopy as a possible rapid tool to evaluate abiotic stress effects on pineapple by-products. Appl Sci 9(19):4141
76. Olale K, Walyambillah W, Mohammed SA, Sila A, Shepherd K (2017) Application of DRIFT-FTIR spectroscopy for quantitative prediction of simple sugars in two local and two Floridian mango (Mangifera indica L.) cultivars in Kenya. J Anal Sci Technol 8(1):1–13
77. Skolik P, Morais CLM, Martin FL, McAinsh MR (2019) Determination of developmental and ripening stages of whole tomato fruit using portable infrared spectroscopy and chemometrics. BMC Plant Biol 19(1):236
78. Olale K, Walyambillah W, Mohammed SA, Sila A, Shepherd K (2019) FTIR-DRIFTS-based prediction of β-carotene, α-tocopherol and l-ascorbic acid in mango (Mangifera indica L.) fruit pulp. SN Appl Sci 1(3):1–11
79. Park YS, Im MH, Ham KS, Kang SG, Park YK, Namiesnik J et al (2015) Quantitative assessment of the main antioxidant compounds, antioxidant activities and FTIR spectra from commonly consumed fruits, compared to standard kiwi fruit. LWT- Food Sci Technol 63(1):346–352
80. Yaman N, Velioglu SD (2019) Use of attenuated total reflectance—Fourier transform infrared (ATR-FTIR) spectroscopy in combination with multivariate methods for the rapid determination of the adulteration of grape, carob and mulberry PEKmez. Foods 8:7
81. Craig AP, Franca AS, Oliveira LS (2012) Evaluation of the potential of FTIR and chemometrics for separation between defective and non-defective coffees. Food Chem 132(3):1368–1374
82. Obeidat SM, Hammoudeh AY, Alomary AA (2018) Application of FTIR spectroscopy for assessment of green coffee beans according to their origin. J Appl Spectrosc 84(6):1051–1055
83. Bernardino-Nicanor A, Acosta-García G, Güemes-Vera N, Montañez-Soto JL, de los Ángeles Vivar-Vera M, González-Cruz L (2017) Fourier transform infrared and Raman spectroscopic study of the effect of the thermal treatment and extraction methods on the characteristics of ayocote bean starches. J Food Sci Technol 54(4):933–943
84. Monje AFB, Parrado LX, Gutiérrez-Guzmán N (2018) ATR-FTIR for discrimenation of espresso and Americano coffee pods. Coffee Sci 13(4):550–558
85. González-Cruz L, Montañez-Soto JL, Conde-Barajas E, de la Negrete-Rodríguez M, Flores-Morales A, Bernardino-Nicanor A (2018) Spectroscopic, calorimetric and structural analyses of the effects of hydrothermal treatment of rice beans and the extraction solvent on starch characteristics. Int J Biol Macromol 107(PartA):965–972
86. Plans M, Simó J, Casañas F, Sabaté J, Rodriguez-Saona L (2013) Characterization of common beans (Phaseolus vulgaris L.) by infrared spectroscopy: comparison of MIR, FT-NIR and dispersive NIR using portable and benchtop instruments. Food Res Int 54(2):1643–1651
87. Gok S, Severcan M, Goormaghtigh E, Kandemir I, Severcan F (2015) Differentiation of Anatolian honey samples from different botanical origins by ATR-FTIR spectroscopy using multivariate analysis. Food Chem 170:234–240
88. Amir RM, Anjum FM, Khan MI, Khan MR, Pasha I, Nadeem M (2013) Application of Fourier transform infrared (FTIR) spectroscopy for the identification of wheat varieties. J Food Sci Technol 50(5):1018–1023
89. Dong D, Zhao C, Zheng W, Wang W, Zhao X, Jiao L (2013) Analyzing strawberry spoilage via its volatile compounds using longpath Fourier transform infrared spectroscopy. Sci Rep 3:1
90. Xiao G, Dong D, Liao T, Li Y, Zheng L, Zhang D et al (2015) Detection of pesticide (Chlorpyrifos) residues on fruit peels through spectra of volatiles by FTIR. Food Anal Methods 8(5):1341–1346
91. Batista NN, de Andrade DP, Ramos CL, Dias DR, Schwan RF (2016) Antioxidant capacity of cocoa beans and chocolate assessed by FTIR. Food Res Int 90:313–319

92. Raba DN, Poiana M-A, Borozan AB, Stef M, Radu F, Popa M-V (2015) Investigation on crude and high-temperature heated coffee oil by ATR-FTIR spectroscopy along with antioxidant and antimicrobial properties. PLoS One 10(9):e0138080
93. Lee B-J, Zhou Y, Lee JS, Shin BK, Seo J-A, Lee D et al (2018) Discrimination and prediction of the origin of Chinese and Korean soybeans using Fourier transform infrared spectrometry (FT-IR) with multivariate statistical analysis. PLoS One 13(4):e0196315