A Review on Food Toxic Identification Using Various Spectroscopic Techniques

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Abstract- Food adulteration is a common and old problem, which can be often seen globally. Adulteration is nothing but adding or deleting some substances in the food contents (eg. Spices, milk) which may arise some serious problems to human health. In this paper, some of the common food toxic contents present in the spices, black pepper, milk and its various spectroscopic identification techniques are discussed. In Electromagnetic spectrum, various spectral wavelengths namely, Ultra violet, Infrared, and microwave radiation are utilized for the identification of adulterants in food products. This paper provide a review about different Spectroscopic analysis which determines the qualitative and quantitative adulteration present in the food substances and these techniques are mostly non-destructive, rapid, and produces better results.

Keywords – Spectroscopic techniques, food and milk adulteration, Machine Learning Techniques.

I. INTRODUCTION

One of the essential needs in everyone's everyday life is food, which plays sustaining role. In earlier days, farmers use to grow organic foods and people use to buy from the market. Later, it changed on nowadays and exploits the agriculture wealth and humans health due to the addition of fertilizers and toxic contents for gaining additional profit by vendors, shopkeepers. Usage and consumption of banned pesticides and harmful chemicals in the fruits and milk products being quite often. It leads to severe issues of the internal organs in human beings. These consequences are matter of concern in present scenario.

Spectroscopy defines an interaction between light matter interaction and process of getting the spectrum. It can also be defined as the study of emission, absorbance and transmittance of light and radiation by the compound of molecules (matter). Mainly the transmittance/absorbance of spectrum works based on the principle of beer-Lambert's law stated as

$$A = € CL \qquad (1)$$

A-Absorbance
€ –Molar Extinction coefficient
C– Light absorption
L - Path length

Based on the method of detecting matters the spectroscopic equipment type is selected. If the matter is soluble, the analysis can begin with ultraviolet- visible spectroscopy (UV-VIS) [1].

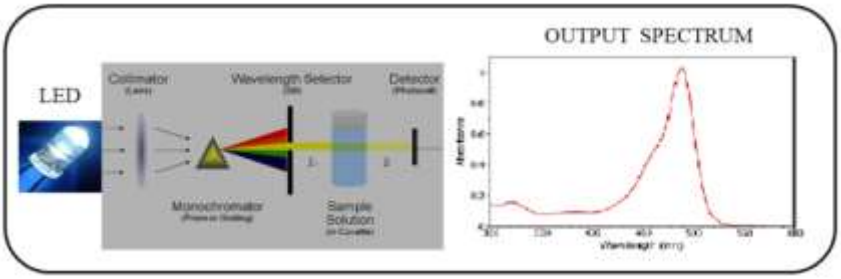

Figure1. Basic Working principle of a spectrometer

The working Principle of spectrometer is to know/observe how much a chemical substance/sample observes the light source and measuring sample light intensity shown in Fig 1. The respective sample may observe or transmit light over a certain range of wavelength and it is showed by a spectrum.

Usual spectrochemical methods comprise of Ultraviolet and visible infrared spectroscopy designed in the range of (200nm to 400nm UV) and (400nm-700nm Visible Range), Molecular Fluorescence spectroscopy(Emission spectra observed,190nm-750nm), IR absorbance spectroscopy(NIR 780-2500nm), Raman spectroscopy(2500nm-20000nm), Fourier Transform Spectroscopy(2000nm-25000nm), and NMR(Nuclear magnetic Resonance) spectroscopy.[1]

Raman spectroscopic techniques mainly involving surface-enhanced Raman spectroscopy (SERS), Fourier-transform (FT) Raman spectroscopy, Near Infrared (NIR) Raman spectroscopy, and micro-Raman spectroscopy for milk analysis including milk compositions, microorganisms and antibiotic residues in milk, as well as milk adulterants [2]

Commercial near – NIR reflectance introduced in 1970s, provided rapid quantitative and qualitative determination of moisture, fat, and protein in cereals grains and other food substances. Nowadays IR spectroscopy comes with quantitative and qualitative analyses of finished foods and ingredients.

IR radiation can also be measured in terms of its frequency , which is directly related to the energy and it is given by the following equation

$$E = h\nu \qquad (2)$$

E = energy of the system

H = Planck's constant

ν = Frequency in hertz

FTIR-Fourier Transform Infrared Spectroscopy has enhanced quality in its spectra and less time to acquire the data [3].

Table1. Methods of spectroscopic analysis techniques

Food materials	Spectroscopic techniques	Average Identification wavelength range	Method of analysis
Milk constituents	Raman Spectroscopic	600-3700 cm^{-1}	Partial least Square modelling
Common Food Adulterants	Fourier Transform-Near Infrared spectroscopic	400- 25000nm	Limit Of detection
Various milk and Food Adulterants	Near Infrared Spectroscopic	400- nm	Support vector Machine, Partial Least Square
Spices adulteration	Terahertz Spectroscopic	3mm-30μm	Support vector Machine

Table 1. show the different adulterant identification methods based on various spectroscopic techniques.

Spectroscopic techniques for identification of food and milk products are listed as

- Terahertz spectroscopy
- Nuclear Magnetic resonance Spectroscopy

- Raman Spectroscopy
- FT-IR

II. REVIEW ON FOOD ADULTERANTS

2. Adulterants

Adulteration says that mixing hazardous or foreign chemical substances to the food materials like in spices, milk etc., to gain extra immediate profit and to increase the quantity of food item which may results in the loss of quality. Food adulteration means that the nourishment product fails to attain the legal standards. For example adding yellow chalk powder on turmeric powder, sugar syrup in honey, and mixing starch, urea, water, formaldehyde, and few more chemical substances are added in the milk to make it appear good, also to maintain its freezing point, and to preserve the milk for long time.

2.1. Common Adulterations In Spices

Introducing adulteration in food can be of two types, one is intentional, which means deliberate addition of inferior substance, makes higher appearance such as Chalk powder in turmeric, papaya seeds in black pepper. Terahertz imaging provide a fairly transparent detection of adulterants in packed foods/ spices, chemicals like hydrochloric acid is used for chalk powder identification in turmeric. Consumption of chalk powder can cause many problems such as nausea, loss of appetite, swelling of the face. Turmeric doesn't have any specific frequencies in the range of 2 to 10 THZ. But with addition of chalk powder, the turmeric powder shows absorption peaks in the range of 3.6 THZ, 6.3 THZ, 7 THZ and 9.3 THZ. From the spectrum it is noted that as the mixture of chalk powder increases the absorption peak increases [4]. Another kind of adulteration is incidental, which means addition of foreign substances such as Larva in spices, fungal infection on contaminated fruits. A non-destructive method of two spoilage microorganisms infections on post harvested strawberry fruit were identified in its earlier stage by VNIR and SWNIR regions of hyper spectral sensors [5].

FT -IR and NIR spectroscopy revealing the adulteration in ground black pepper. A Total of 115 samples (30 pure, 48 spiked) black pepper from various countries were analyzed in this study. The adulterants mixed are pinheads, husk, oleoresin and spent materials. These adulterants were identified by FT-IR spectra in the respective diagnosis bands of 996 – 1633cm^{-1}. Using NIR model, 100% of correct classification were made in identifying the different types of adulterants. By using FT-IR model, about 92-100% of correct classifications were made [6]. Cassava starch and corn flour are the specified adulterants present in cumin and black pepper powder which are being identified through the NIR spectroscopic and chemo-metric model analysis. A total of 90 black pepper samples and 40 cumin seeds were investigated. SIMCA (Soft independent modeling of class analogy) involves binary and multivariate analysis and produces genuine classification on black pepper and cumin samples of about 100% and 92% correct classification for the unadultered samples [7]. Some of the other spectroscopic techniques are available to determine the qualitative and quantitative concentration of toxic contents in the food.

2.2. Adulterants in milk

Milk if the primary source for all living beings in the globe. It contains fat globules, proteins, minerals, vitamins, calcium, nitrogen and lactose rich liquid food [8]. Few adulterants are added in the milk to increase its quality in fraudulent way and to increase the storage period of milk. Some of the adulterants namely urea, starch, sodium salicylate, formalin, hydrogen peroxide, ammonium sulphate, and water etc., added in the milk in an dishonest way to enlarge its quantity, and appearance. There are many spectroscopic techniques available to identify the adulterants in the milk sample. One among the technique is employing signal generator generates frequency of 0.5MHZ and is transmitted, the transmitter signal pass through the milk sample (one adulterated with simple tap water and second adulterated with synthetic milk) and received by the receiver and analyzed by digital storage oscilloscope.

The results show that with increase in adulteration the voltage level of the signal increases. The result is to ensure to control the quality and properties of milk products [9]. Another study illustrates, that the detection of multiple adulterants in milk with 10 various adulterants in different quantities and the test was conducted using MID- IR spectroscopy and SIMCA technique. One class modeling was done for pure milk with sensitivity of 93.1%.Then

multiclass modeling was implemented for 5 effective adulterants and results obtained with 82% correct classification, 17% of inconclusive and 1% misclassified. It produces an efficient result for the analysis of numerous samples, lowering the risk of error and reduced experimental time [10].

One another work indulges in detection of cow whey adulterant mixture in buffalo mozzarella. A training set of calibrators consisting of 7 series of 17 buffalo/whey mixtures with increasing percentages of cow whey. The rapid, robust ,capillary electrophoresis method for quantifying and detecting the mixture of cow alpha- lactalbumin adulteration in buffalo milk produces output with linearity of $R^2 = 0.968$, and for different bovine whey mixtures ratios obtained various relative standard deviation. Thus the results concluded with detectable fraudulent on cow milk was 1% and Quantification was 3.1% [11]. Furthermore, the works on quantitative identification of urea and starch adulteration in milk using electrical impedance between sensors measurements. Impedance analysis shows that adulteration changes found mostly in the resistive part of the electrical impedance. The frequency range of 90KHZ performs well for the milk adulteration identification. The results also states that, as the concentration of adulteration raises with decrease in its pH, voltage value, and conductivity [12].

Common parameters used to check the quality of milk are Fat percentage, SNF (Solid-Non-Fat), Protein and Freezing point. Mainly, the freezing point test conducted for identification of added water in the raw milk. An instrument was developed to obtain the measurement of substance concentration based on NIR diffuse reflection. To validate this developed mechanism an experiment was conducted to detect the adulterant in milk, especially for water diluted milk content. The results showed 99% of accuracy in identifying the water diluted milk. It is non-destructive, fast and widespread method for compound identification, but failed to validate for other adulterants. [13].

A prototype able to measure the intensity of IR scattered light from the raw milk samples. This method identified the added water in the raw milk. The resultant determination index of 0.932 and (Root Mean Square Error Of Prediction)RMSEP=0.0267[14]. Another method developed using Electrical impedance spectroscopy (EIS) technique and employed to identify and to quantify the percentage of soap weights in three various cow milk samples. The results showed that a steady variation present in the impedance, current, conductance and capacitance with the measured addition of soap in the milk, and this method also able to detect the presence of >= 0.1% soap in the milk, and it is applicable effectively about 0.9% [15].

Next, a classification made between authentic, adultered skim and nonfat dry milk powder done through solution – state, high field ^{1}H NMR(1 hydrogen nuclei- Nuclear Magnetic Resonance) spectroscopy combined with conformity index , non targeted method based analysis. It supports in finding the root cause analysis of suspicious results and support milk powder authentication and adulterant detection.The results shows detection of adulteration was found to be high for lowest concentrations about(>=0.005-0.05%w/w) for small molecule, nitrogen rich samples [16].

Electroanalytical cyclic voltammetric test with chemometrics analysis employed for detection and quantification of adulteration of fresh milk with reconstituted skim milk powder. The fresh cow milk samples tested under Multivariate analysis,and the obtained the adulterant detectable observed predicted values about 100%(volume/volume) [17].

To overcome the blending effect on the adulterated milk powder samples MIR analysis were made, and utilized adulterants are ammonium sulphate, cornstarch and semicarbazide hydrochloride .Wet and dry- blended adultered samples tested on MIR measurement and classified on one-class classifier SIMCA(Soft Independent Modelling by Class Analogy) model for reconstituted skim milk. The results shows that < 5% of fraud levels could be detected [18].

Identification of detergent in milk samples can be able to predict using Near infrared spectroscopy, the analysis made through principal component analysis, the results shows that the validation test output is 93% and the calibration test produces 99% output [19].

An another rapid method for identification and quantification of five different milk adulterants were analysed by MIR-spectroscopy and SIMCA(Soft Independent Modeling for Class Analogy) and Partial Least square Regression allows better discrimination of controlled milk samples. The result says that this method gives an better alternative for screening potential crooked practice [20].An rapid untargeted sreening of Laser Direct Infrared(LDIR) imaging system assessed a study on adulterant identification ,detection and semi – quantification in food ingredients in dry and wet blended food samples. The results of LDIR screening analysis for economically motivated adulteration (>5%) in food materials were assessed.The dry blending adulteration method achieves 100% of sensitivity and selectivity in the presence of nitrogen-rich compounds and bulking agents, and also if the adulteration level is higher than 5% it achieves the detection rate of 98% to 99% of sensitivity [21].

Another low-cost NIR digital photometer prototype developed for detection of water adultered in milk. This equipment measures the transmitted IR radiance from the 0 to 25% of added water in the raw milk using the

method of cryoscopy and assessment made with the above developed prototype. Results showed that the measurement of percentage of added water ,mean absolute error rate is less than 1%, by doing repeatability with 2 sets of ten measurements obtained deviations to less than 0.7% of mixed water, this method achieves better results at faster rate when compared with commercial cryoscopy [22].

IV.CONCLUSION

Adulterations in food substances are unavoidable, so it can be controlled and detected using several spectroscopic techniques. This review paper mainly discusses various non-destructive, rapid analysis methods for identification of toxic contents in spices and milk samples. Among which FTIR and NIR produces effective results for liquid foods. Some of electrical impedance measurements also gives better ouput in predicting the adulterants. However, this low cost ,Low power consumption device will revolutionize the use of spectroscopic techniques for measuring the adulterants in food substances in near future.

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