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Determination of Adulterants in Food: A Review

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ABSTRACT

This paper proposes the use of the least-squares support vector machine (LS-SVM) as an alternative multivariate calibration method for the simultaneous quantification of some common adulterants (starch, whey or sucrose) found in powdered milk samples, using NIR spectroscopy with direct measurements by diffuse reflectance. Due to the spectral differences of the three adulterants a nonlinear behaviour is present when all groups of adulterants are in the same data set, making the use of linear methods such as partial least squares regression(PLSR) difficult. Chemo metric MID-FTIR methods were used to detect and quantify the adulteration of mince meat with horse meat, fat beef trimmings, and textured soy protein. Also, a SIMCA (soft independent modelling class analogy) method was developed to discriminate between adulterated and unadulterated samples.Near-infrared (NIR) spectroscopy combined with chemo metrics methods has been used to detect adulteration of honey samples. The results showed that WT-LS-SVM can be as a rapid screening technique for detection of this type of honey adulteration with good accuracy and better generalization. Partial least squares (PLS) were employed for the analysis of Fourier transform infrared spectroscopy (FTIR) spectral data of the blend oil samples.

Key Words: Adulterant, Estimation, Food Products.

INTRODUCTION

During the last fifty years there has been a lot of emphasis on the quality and safety of the food products, of the production processes and the relationship between the two [1]. These requirements call for on line detection techniques which have the following advantages: (i) can be assembled in the production line and take place under realistic environment, (ii) early detection of possible failures, (iii) permanent monitoring of the conditions, (iv) assessment of conditions at any desire time [2]. These advantages enable detection of quality changes of raw materials and final product under steady process conditions compared to other non-destructive

techniques, NIR spectroscopy does not need any sample preparation. Hence the analysis is very simple and rapid, which is a requirement for online application. Furthermore NIR technique allows several constituents to be measured simultaneously. Finally, the relatively weak absorption due to water enables high-moisture foods to be analysed [3]. The use of multivariate calibration methods in modeling near infrared spectroscopy data is widely employed, being considered a standard procedure for quantitative analysis using this spectroscopic technique. Partial least squares regression (PLSR) [4] is the most commonly used multivariate calibration method. Neural networks [5, 6] based on multilayer perceptrons have been used with relative success. However, neural networks suffer critical drawbacks due to the gradient based training methods employed that lead to the existence of many local minima, and the final solution in many instances is not reproducible.

Recently, a promising methodology called support vector machines (SVM) [7-8] has been introduced to perform nonlinear classification and multivariate function estimation or nonlinear regression. Minced meat production removes the morphological characteristics of muscle, making it difficult to identify one type of muscle from another [9]. Honey has a wide range of applications in food industry. It can be processed for direct consumption or used as ingredient in various processed food products. Because of its nutritional value and Unique flavour, the price of natural bee honey is much higher than that of the other sweeteners, such as refined cane sugar, beet sugar, and corn syrup; therefore, is susceptible to be adulterated with these cheaper sweeteners. Adulteration of honey is in constant progress and has been reported in various occasions [10]. Conventional analytical methods for measuring the oxidation and adulteration of oil are time consuming, destructive, expensive, require chemical reagents, and are laborious. NIR spectroscopy technique has many applications in this area [11]. All these properties make NIR technique widely acceptable in recent years as one of most promising on/in-line detection methods in food and other areas. Industries involved with foods and beverage have traditionally used NIR measurements for quality control, blending, and process control [12]. Developments in computer science and chemo metrics have prompted parallel developments in the on/in-line NIR techniques, and have attracted considerable attention from food researchers. For example, this technique was applied for on-line detecting fat, moisture, and protein content during meat process [13].

Dairy products

Dairy products are classified in to i) common milk ii) powdered milk. Powdered milk enjoys an excellent reputation as a good source of nutrition and is also of great economic importance. Besides the large consumption of powdered milk in the retail sector, this type of milk is widely used in school meals. Investigation of milk authenticity is extremely important, in both economic and public health terms.

In Brazil, the fifth largest milk producer in the world and has 4.3 % of global consumption [14], until recently, liquid milk used to be the major target of food frauds. Liquid milk can be adulterated with water, neutralizers to mask acidity, salt or sugar to mask extra water or high solid contents, cheese whey, among others [15], recently, the phenomenon of adulteration of powdered milk has increased in many parts of Brazil, aided by the problem that the detection of the adulterants is difficult using a single test. The most frequent contaminations consist of the addition of whey, which is 90% cheaper than milk and usually imported from Argentina, New Zealand or Australia. Other common contaminants are starch, sucrose, less frequently, maltodextrine and sodium hydroxide .usually, the contaminants range from 20 to 25%, which

does not cause detectable flavour changes, however, contamination rates may correspond to as much as 60%.

Starch is combination of two polysaccharides: amylose and amylopectin [16] and contents vary between species, different cultivators of the same species and also with plant maturation. The iodine reaction coupled with potentiometric or aerometric titration [17] is still the method usually employed for starch determination in milk.
Whey despite its noble uses, whey is often discarded by the dairy industry during cheese making and, due its economic feasibility. It is used as an adulterant of both fluid and dry milk. Whey can be detected by analysing its caseino macro peptide (CMP) or glycol macro peptide (GMP) contents [18] using chromatography [19] or electrophoresis [20, 21], which requires considerable time for preparation and analysis. Currently the qualitative analysis by HPLC has been implemented. HPLC cannot detect whey produced by the direct acidification of milk (22).

Sucrose, the major source of sucrose are sugar cane and sugar beet, and it is certainly the most important disaccharide , due to the amount and frequency with which it is found in nature, and also to its importance to human nutrition. A method for the qualitative and quantitative analysis of disaccharides is HPLC with detection by refractive index (IR) [23]

Meat and meat products
Meats are very susceptible to spoilage and are also expensive as compared to other food types. Hence, there has been considerable interest in measuring their composition and quality, in order to improve the efficiency of unit operations applied in meat processing [24]. From an industrial and marketing perspective, the major raw materials in the processing of meat are carcasses of beef and pork. Minced meat productions remove the morphological characteristics of muscle, making it difficult to identify one type of muscle from another. For this reason meat substitution with unspecified species, usually of lower quality, is the most common form of economic adulteration in the minced meat industry, constituting a fraudulent act that could have economic and health repercussions [25]. This is a concern for importation and the meat packer, but also at the restaurant and retail level where the substitution is easier to conceal. Meat species adulteration concerns consumers in terms of economic loss, food allergies, religious observance, and food safety [26]. Also, since 1960, textured soy protein has attracted attention as a cheaper protein than meat; therefore substitution of minced meat with soy protein is another economic fraud. Species substitutions, such as substitution of horse meat for beef, pork and sheep meat, have been reported in several countries.

Some methods for detection of meat adulteration have been comprehensively reviewed by Hsieh (2000), among these: (1) capillary electrophoresis was reported to identify raw meat species; however, it was difficult to interpret the results when mixtures of more than one species or protein additives were involved [27]. (2) Chromatographic methods such as gas chromatography, liquid chromatography, and HPLC have been applied to identify species based on fatty acid composition [28]. (3) Polymerase chain reaction (PCR) methods such as the random amplified polymorphic DNA fingerprints [29], an acting gene PCR [30] and multiplex PCR [31] have been reported for the detection of species adulteration. (4) Immunological methods are suitable for assaying various analytes in complex mixtures.(5) NIR spectroscopy technique had not been used for on/in-line detection of meat until 1996. The first online application of this technique reported for determination of fat, moisture, and protein contents in ground beef [32].

Honey

Honey is a naturally sweet and viscous product produced by Apis Mellifera bees from the nectar of flowers, from secretions of living parts of the plants, or excretions of plant-sucking insects on the living part of plants that the honey bees collect, transform, and combine with specific substances of their own, deposit, dehydrate, store and leave in the honey combs to ripen and mature [33]. According to the European Union regulations, the codex alimentarius of the food. Agriculture organization of the United Nations and other various international honey standards (official general of the European communities, 2001; codex alimentarius commission standards, 2001), "honey stipulates a pure product that does not allow for the addition of any other substance". Bee honey is a unique sweetening agent that can be used by humans without processing and have significant nutritional and medicinal benefits. It is a rich source of readily available sugars, organic acids, various amino acids and in addition source of many biologically active compounds. China is both a large honey producer and exporter in the world. China's varieties of honey are shipped all over the world. Honey has a wide range of applications in food industry. It can be processed for direct consumption or used as ingredient in various processed food products. Because of its nutritional value and unique flavour, the price of natural bee honey is much higher than that of the sweeteners, such as refined cane sugar, beet sugar and corn syrup; therefore, is susceptible to be adulterated with these cheaper sweeteners.

Detection of adulteration of honey is done using different analytical techniques such as isotopic [34], chromatographic [35], thermal analysis [36] and trace element techniques [37]. FTIR spectroscopy in combination with multivariate statistical techniques (chemo metrics) makes possible to obtain specific information about different parameters simultaneously in a direct, reliable and rapid way. Its use to evaluate the authenticity of food products has been reported before.

FTIR chemo metric technique requires low sample volume and is environmental friendly, due to the fact that minimal or no sample preparation is required, which greatly speeds up sample analysis [38].

Constrains of NIR techniques in food analysis

Although the operating cost of NIRS is low, the instrument itself is highly priced; this limits its practical application. Efforts by researchers and industrial organizations to develop simple and low-cost instruments could revolutionize the use of NIR techniques for on/in-line quality monitoring of foods.

Some calibration models based on NIR spectroscopy, especially for on-line application, are not reliable and stable enough when used practically. Hence, it is imperative for researchers to choose proper chemo metrics to build robust models. In some cases, conventional methods may not offer a satisfactory solution to a given problem due to complexity of the data. This also necessitates the development of new chemo metric methods so as to further improve the reliability and accuracy of the calibration models.

In addition, there are other limitations of NIR spectroscopy technique. The technique is not sensitive to the mineral content, since there is no absorbtion of minerals in the NIR spectrum region. An alternative way to solve this problem efficiently is to combine different detection techniques with NIR spectroscopy, such as X-ray fluorescence spectroscopy, UV light, and electronic nose technique. Some papers describing the use of a combination of techniques using different detection methods have been published in recent years [39], although more efforts should be made to solve this issue.

Olive Oil

Olive oil is an economically important product in the Mediterra-gjui countries. It has a fine aroma and a pleasant taste, and is internationally appreciated for its nutritional value and health benefits [40]. Costs of virgin olive oil are high when compared to other commonly used vegetable oils, making it prone to adulteration with less expensive oils in order to increase profits. Most common adulterants found in virgin olive oil are seed oils, such as sunflower, soy, corn and rape-seed oils as well *as* nut oils, including hazelnut and peanut oils [41].

Several commercial categories of olive oil are legally defined by the European Community Council of Regulation (EC, 2001), which are marketed with different prices. Thus, there is also the possibility of mixing less expensive commercial categories such as refined olive oil and pomace oil with the highest quality product, extra virgin olive oil (EV00), for economic reasons. Detection of these two types of adulteration is often complicated with no single test available that can accomplish the task, especially when oils with chemical compositions similar to EVOO are employed [42].

Detection and determination of the adulteration of EVOO are not simple tasks; efforts to detect and determine adulteration traditionally demand monitoring of several organic compounds to establish a comparison with typical unadulterated oils in order to identify change of composition that could be related to adulteration. In this respect, the detection of characteristic chemical components has been proposed as a suitable indication of the presence of other oils in EVOO [43], but the use of such compounds to discover adulteration, when refined oils are involved, is quite difficult. In addition, chemical methods traditionally employed for the control of authenticity of virgin olive oil as gas chromatography and high performance liquid chromatography are expensive, time-consuming, require skilled operators and have high environmental impact [44].

New and complementary analytical techniques devoid of such troubles, could act as supporting tools for currently used methods, being very helpful to improve the detection of EVOO adulteration. Among them, calorimetric techniques seem to be very promising and the application of differential scanning calorimetry to make evident the adulteration of EVOO was recently reported by Chiavaro and co-worker [45]. On the other hand, nuclear magnetic resonance coupled with multivariate statistical analysis [46] was successfully applied to detect EVOO adulteration with Iampante olive oil and refined olive oil.

Spectrofluorimetric methods are also emerging as an important alternative; in fact, excitation-emission fluorescence spectroscopy [47] was reported for detecting adulteration of olive oil. FTIR has been also successfully used to detect olive oil adulteration [48] and freshness [49]. The latter technique is often coupled with chemometrics methods such as principal component analysis (PCA), linear discriminant analysis (LDA), support vector machine (SVM) and K-nearest neighbor3 (KNN) [42], that can be used to assign the measured spectrum to a category in a training set. In addition, quantitative chemo metrics strategies are suitable for analysis of complex mixtures as they enable rapid and simultaneous determination of each component in a mixture without time-consuming separations and with minimum sample preparation. Among such methods, partial least squares (PLS) is a factorial multivariate calibration method that decomposes spectral data into loadings and scores, building the corresponding calibration models from these new variables [50]. This method, which requires analytes compliance of Beer's Law, has been repeatedly coupled with FTIR spectroscopy and extensively used to obtain different quality parameters of edible oils [51]. Particularly, FTIR-PLS has been recently applied to the evaluation of the fatty acid composition and other quality parameters of virgin olive oil [52].

CONCLUSION

The aim of the present work is to develop a new application of the analytical method association as a rapid, inexpensive and non-destructive authenticity measuring tool, useful to determine the adulteration in food and food products and also to identify and quantify the percentage of the ruining agent in the blend. The results demonstrate a better prediction ability of the LS-SVM technique to determine starch, whey or sucrose in powdered milk samples. The most important advantages were the capacity of the LS-SVM to predicts the absence (not the presence) of adulterants in the samples, while the PLS models may give false positives. LS-SVM is a promising technique to be used for estimation of the quality to the products from indirect, but fast and reliable measurements, such as near infrared spectroscopy. By use of ATR mid infrared Fourier transform spectroscopy it has been possible to successfully quantify the content of adulterant (corn syrup, HFCS and inverted sugar) in honeys. The superiority of LS-SVM in building models with better generalization abilities than those obtained from SVM, BP-ANN, KNN, and LDA for the problem studied. The recognition ratio of 95.2% and AUC of 0.952 by WT-LS-SVSM model was achieved for the test set. The results showed that NIRS has the potential ability to detect sugar adulterants in honey.

FTIR-PLS to determine the EVOO approach represents a facile and convenient means for monitoring olive oil quality with the advantage of ease of operation, high sample turnover and no sample pre-treatment.

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