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Novel method for vegetable oil type verification based on real-time microwave sensing

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ABSTRACT

A novel monitoring approach that allows real-time identification of the vegetable oil types is reported. Unlike other available detection methods, which are only lab based, this developed technique exploits a low-power microwave sensing principle and provides for cost-effective, portable, on-the-spot verification of the cooking oil type, which is vital not only for compliance with Food Information Regulation, but for consumer safety, food quality monitoring and customs control. In particular, a response of a sensor on its own, without any oil sample in contact, displays a resonant peak at 7.81 GHz, but it shifts to lower frequencies of 6.92 GHz, 6.81 GHz, 6.73 GHz and 6.62 GHz when in contact with Filippo Berio Gusto Fruttato oil, Filippo Berio Extra Virgin Olive oil, Don Mario oil and ASDA Refined Olive oil accordingly.

1. Introduction

Especially in the last few years, cheap adulterated vegetable oils from developing countries markets are increasingly putting at risk the health of consumers all over the world, with Europe in particular bearing the burden of ensuring the food safety and quality. Adulterated vegetable oils result from fraudulent substitution practices in which inferior and superior quality oils are mixed. The new Food Information Regulation (FIR) 1169/2011, adopted by the European Union at the end of 2011, was specifically designed to make food labelling easier to understand for consumers. One of the main points in the FIR is that the types of vegetable oil used in food, such as palm, rapeseed, sunflower or corn oil blends, must be stated within a generic 'vegetable oil' declaration. This is believed to promote efficient quality control, falsification repression and product standardisation.

Notably, the European Communities regulation (ECC/640/2008) grades virgin olive oils in three categories based on their organoleptic characteristics: extra-virgin (EVOO), which has the best quality and no undesirable sensory descriptors; virgin (VOO), which allows negative sensory attributes with low intensity ($\leq$3.5); and lampante (LOO) olive oils, which have high intensity defects (3.5) [1].

Because of its financial importance and role in the diet, olive oil has been investigated for other purposes, such as the identification of defects (e.g. rancid taste, presence of vegetable water or muddy sediment), pollutants (e.g. pesticides or metals) or fraud (e.g. mixing with hazelnut oil) using various analytical approaches, as discussed below. Different chemical compounds are responsible for the olive oil aroma. These volatile compounds, such as aldehydes, aliphatic and aromatic hydrocarbons, aliphatic and triterpenic alcohols, ketones, acids, esters, ethers and furan and thiophene derivatives, are formed during the olive oil extraction process [2]. The analysis of the olive oil organoleptic characteristics is usually carried out by two procedures: the sensory panel test and the study of the volatile compounds [1]. Both of these methods are time consuming, labour expensive and cannot be adapted for the online real-time monitoring of oil quality.

For example, palm oil has become one of the important edible oils and besides its nutritional and medicinal value, it is increasingly popular as a raw material for the oleochemical industries and a fuel for automobiles. Palm oil is obtained from the mesocarp of the oil pahn fruits and oil quantity is determined by the quality of fruits during harvesting or amount of oil, water and free fatty acid (FFA) in the fruit [3]. At 20 weeks after anthesis, only a small amount of oil increases and at the same time the percentage of FFA in oil increases, which reduces the quality of oil. The fibre content in mesocarp is almost constant after a certain stage of maturity whereas water and oil vary with ripeness. Therefore, there is an optimum time by which the bunch should be harvested. The close

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relationship between MC and stage of ripeness gives a possibility of using this parameter to gauge the ripeness of the fruit and as a consequence the quality of the oil.

Foods can contain a complex mixture of saturated, monounsaturated, and polyunsaturated fatty acids, each with a variety of carbon chain lengths. Various identification and quality control methods of vegetable oils are based on conventional methods for the determination of acid index, ratios of unsaturated to total fatty acid content, saponification, iodine and refraction indices, as well as triacylglycerol determination [4].

Available standard methodology for analysis of vegetable oil is Fatty Acid Methyl Esters (FAME). Alternative techniques that may be employed for the determination of oil type of unknown samples include: gas chromatography, gas chromatography–mass spectrometry, high-performance liquid chromatography (HPLC); size-exclusion HPLC; differential scanning calorimetry, infrared spectroscopy, supercritical fluid chromatography, thin layer chromatography, ultraviolet spectroscopy, fluorescence spectroscopy, isotope radio mass spectrometry, gravimetry and the emulsion stability of nitromethane/vegetable oil method [5].

One of the most powerful modern methods of oil quality verification is the fingerprints method, acknowledged for its specificity. In the last few years, attention has been focused on authentication for genetic varieties of olive oils using nuclear magnetic resonance (NMR) fingerprinting [6]. It consists of selecting a known compound or a marker as qualitative and quantitative target to assess authenticity and inherent quality [7]. Several attempts have been made in order to verify the declared geographical origin of olive oils by means of suitable chemical parameters, such as triglyceride and fatty acid profiles or by means of NMR [8] and ^{1}H NMR spectroscopy [9]. NMR has been used for the prediction of the olive oil geographical origin using a fingerprinting approach, where the spectra are used as a whole (fingerprint) without assigning particular resonances and thus obtaining a comprehensive, multivariate, description of the analysed samples. ^{1}H NMR fingerprints of virgin olive oils (VOOs) from the Mediterranean basin were analysed by principal component analysis (PCA), linear discriminant analysis (LDA), and partial least-squares discriminant analysis (PLS-DA) to determine their geographical origin at the national, regional, or PDO level [10]. ^{1}H NMR fingerprint studies of the unsaponifiable fraction extracted from VOOs was also carried out in order to evaluate the authenticity of olive oil produced in Spain, Italy, Greece, Tunisia, Turkey, and Syria using several pattern recognition techniques [11,12].

However, these techniques usually require time-consuming measurements, sample preparation and qualified staff. Consequently, there is the necessity of quick and simple methods to characterise the origin and quality of vegetable oils and the research is on-going.

Promising alternatives to the methods listed above are DNA fingerprinting identification and electronic nose (E-nose) sensing technology [13], but these methods are still being developed. The couple of gas chromatography with mass spectrometry has resulted in separation and identification of various volatile compounds (aroma) in foodstuffs and these are considered as a key characteristic in many quality control and identification methods of food products by electronic nose sensing techniques of identification of vegetable oils [14,15].

Notably, electronic nose and electronic tongue, combined with pattern recognition techniques, offer a fast, simple and efficient tool for classification purposes. The electronic nose consists of an array of gas sensors, a signal collecting unit and pattern recognition software. The interaction of volatiles on the sensing element causes changes in electrical resistance of the sensor, and since sensor kinetics is different, the data produced are converted into an odour fingerprint which can be interpreted with the use of appropriate mathematical techniques [16]. The principle involved in the electronic nose is the transfer of the total headspace containing different chemical volatile compounds to a sensor array, where each sensor has partial specificity to a wide range of aroma molecules [8].

There are a number of recent reports on the applications of different prototypes or commercial electronic noses and e-tongues [17] for virgin olive oils differentiation, with most of the systems using conductometric chemo-sensors, mainly commercial metal oxide semiconductor or conductive polymers sensors [18–20]. A prototype of electronic nose using a sensor array with 16 sensor heads based on conducting polymers purposely designed for the detection of olive oil aroma has been successfully used for the discrimination of very similar types of oils whose only difference was the geographic origin inside a small area [19].

Another electronic nose system used for the classification of vegetable oils was reported in [21], where different supervised pattern recognition treatments were applied. The system comprising six metal oxide semiconductor sensors generated a pattern of the volatile compounds present in the samples. Feature selection techniques were employed to choose a set of optimally discriminant variables. The K-nearest neighbours (KNN), linear discriminant analysis (LDA), quadratic discriminant analysis (QDA), soft independent modelling of class analogy (SIMCA) and artificial neural networks (ANN) were applied to model the different classes. The results obtained indicated good classification and prediction capabilities, the neural networks being those that afforded the best results [21].

Quartz crystal microbalance (QCM) sensors array were used for the discrimination between different virgin olive oil categories in [22], where the potential of this instrument to olive oil classification between edible and non-edible olive oils, according to their chemical and sensory characteristics, was demonstrated. The percentage of correctly classified samples in relation to the quality parameters (acidity, peroxide value, UV spectrophotometry and sensory evaluation) was 91.7%. Therefore, this process was suggested to be used on-line to separate, in different oildrums, virgin olive oil samples with defects from others without negative sensory properties, as a primary classification of the samples. An array of five QCM sensors (coated with OV-17, OV-275, PEG, Vaseline and Span 80 chromatographic adsorbents as sensing thin films) simplified its construction thus reducing the cost of sensors preparation and maintenance. Indeed, sensors useful life is longer than 10 months, so they can be used during one olive harvest season without the need of being replaced. This new approach could offer a valid alternative to the difficult and time-consuming official olive oil sensory evaluation, and could be a useful tool for on-line separation, before storage, between LOO from these virgin olive oil samples that do not need refining and can be directl y consumed.

Although the above named methods of oil quality verifications are regularly used in various industrial processes, they are bulky, expensive, time-consuming and more importantly, they do not provide adequate information on the composition of the oil being tested if a number of unknown components in unknown proportions is present.

This paper reports on a novel monitoring approach based on electromagnetic field sensing that allows real-time identification of the vegetable oil types. Unlike other available detection methods, which are only lab based, this developed technique exploits a low-power microwave sensing principle and provides for cost-effective, portable, on-the-spot verification of the cooking oil type, which is vital not only for compliance with FIR, but for consumer safety, food quality monitoring and customs control.