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Emulsion Stability and Vegetable Oil Identification and Adulteration

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ABSTRACT

The emulsion stability of nitromethane/vegetable oil is use for the rapid identification and quality control of vegetable oils. Using a volume ratio of nitromethane to vegetable oil of 3:7, the emulsion stability of nitromethane/vegetable oil increases in the following order: nitromethane/palm oil, nitromethane/peat-nut oil, nitromethane/corn oil, nitromethane/soybean oil and nitromethane/sesame oil. The nature of vegetable oil influences the emulsion stability. Falsification of sesame oil with 10% corn oil or any cheaper vegetable oil decreases significantly the stability of nitromethane/sesame oil emulsion. These results indicate that the method could be used for rapid identification and quality control of vegetable oils.

Key words: Vegetable oils, adulteration, identification, emulsion

INTRODUCTION

During these last ten years adulterated vegetable oils become more and more present at low cost in many markets of developing countries. These adulterated vegetable oils resulted in fraudulent substitution practices in which inferior quality edible oil is mixed into superior quality edible oil. All fields of human nutritional activities in developed and developing countries are concerned by fraudulent substitution practices many years ago. Thornton (1968) reported that the first case of fraudulent substitution in food products namely in meat industry was recorded in thirteenth century A.D. at Florence in Italy. While considering the quality of food products from industrial origin, several analytical techniques have been developed to fight against fraudulent substitution practices (Christopoulou et al., 2004; Makkar et al., 2002; Ebbehoj and Thomsen, 1991; Chikuni et al., 1990; Wintero et al., 1990; Patterson and Spencer, 1985; King, 1984). One of the most recent powerful methods to fight against fraudulent substitution practices because of its specificity is the fingerprints methods. These methods consist of selecting a known compound or a marker as qualitative and quantitative target to assess authenticity and inherent quality. The evaluation of this compound in its entirety, so-called fingerprints is widely used for authentication and quality control (Giri et al., 2010; Andola et al., 2010; Wechgama et al., 2008; Bounphanousay et al., 2008; Ratchadaporn et al., 2007; Zhang et al., 2006).

The worldwide economy stipulated nowadays requires that developing countries acquire or develop more and specific production tools for efficient quality control, falsification repression and production standardisation. Quality control of vegetable oils concerned in the present work is one of the many problems to be solved in developing countries exposed to various internal and external

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falsifications of consumer goods. Unequivocal or specific identification of food products in general and vegetable oils in particular remains a challenge as well as on the economic, food and sanitary point of view. Numerous identification and quality control methods of vegetable oils are developed in the literature: conventional methods based on the determination of acid index, ratio of unsaturated to total fatty acids content, saponification index, iodine index, refraction index, triacylglycerol determination (Farhad et al., 2009; Aparicio and Aparicio-Ruiz, 2000; Tian and Yu, 1990; Lyapkov et al., 1988; Gunstone et al., 1986). The coupling of Gas Chromatography (GC) with Mass Spectrometry (MS) have resulted in separation and identification of various volatile compounds in foodstuffs (Wu et al., 2004; Vreuls et al., 1991). These many volatile compounds currently called aroma, are considered as a key characteristic in many quality control and identification methods of food products by new electronic nose sensing technique of identification of vegetable oils (Gan et al., 2005; Guadarrama et al., 2001; Gardner and Bartlett, 1994). All these methods are time consuming and require complicated procedure and equipments. The aim of the present work was to develop a rapid and simple method of quality control and vegetable oils identification.

MATERIALS AND METHODS

Principle of the method: The new analytical procedures used in foodstuffs analysis are generally based on the emission and/or detection of an electromagnetic signal (IR, UV, Visible light) in order to rapidly obtain the response. In fact, the measurement of physical parameters takes place more rapidly than the chemical parameters. Oils that are esters of fatty acids should have as these fatty acids, characteristic superficial tensions that allow the formation of emulsions having well determined properties in relation to the emulsifier considered. The first step of the present method is formation of nitromethane in oil emulsion, in order to be able to better interpret the emulsion properties in the second step. One of these properties, the emulsion stability is evaluated by its time or speed of demulsification using an infrared transphotometer. The principle of this apparatus is based on the reduction of the beam of infrared rays to be propagated through a disperse medium (Bitjoka et al., 1999; Bitjoka and Tchatchueng, 2000). The transphotometer emits a spectrum of near-infrared rays. The emitted spectrum on a path length of 1 cm neither reduces in the oils studied here, nor in the emulsifier used. It has the advantage of being conceived for the study of dispersed media like emulsions, being portable and economically within the means of small industrial units of developing countries.

Materials: Vegetable oils used such as sesame oil, groundnut oil, maize oil, soybeans oil and palm oil were bought from the Ngaoundéré market, or extracted and refined in the laboratory. The emulsifier (nitromethane) of 99% purity, with boiling point of 99°C, refractive index of 1, 3821 and density of 1, 13 was obtained from Hoesch (Germany) and used just after receiving it. The IR transphotometer described by Bitjoka *et al.* (1999) was used in this experiment.

Experimental procedure: In a quartz cell or glass tube of 1 cm path length, introduce with the help of an Eppendorf micropipette of 100-1000 µL, emulsifier and oil in a volume ratio of 1:2 and close quartz cell or a tube using an appropriate safe attached lid. The closed tube is placed on a perking-Elmer micro vibrator, shaking for 3 min and then the tube is immediately introduced in the transphotometer. The response of the transphotometer that is an electric tension, proportional to the intensity of the beam of infrared rays transmitted across the tube was measured after each minute. Three types of data were performed:

- The response of the transphotometer in relation to emulsifier/oil ratio: In order to confirm the variation of the stability of an emulsion in relation to the ratio of its components sesame oil was used
- The response of transphotometer in relation to the nature of oil: Sesame oil, soy bean oil, groundnut oil, maize oil and palm oil were studied with emulsifier/oil ratio of 1:2 to verify the principle of the proposed method
- The response of transphotometer in relation to adulterated sesame oil by groundnut oil: Soybean oil and palm oil

RESULTS

Effect of emulsifier/oil ratio on the emulsion stability: Figure 1 shows the results obtained with sesame oil for the emulsifier:oil ratio of 1:1, 2:3 and 3:7. As can be seen in Fig. 1 the emulsion stability of nitromethane/sesame oil represented by the slope of each line (demulsification speed) increases (demulsification speed decreases) when decreases emulsifier/oil ratio.

As expected, the volume ratio of emulsifier is an important factor on the emulsion stability. The volume ratio of emulsifier to oil of 3:7 was chosen according to these results when studying the emulsion stability and the nature of vegetable oil.

Effect of the nature of vegetable oil on the emulsion stability: The results of the effect of the nature of vegetable oil on the emulsion stability are represented in Fig. 2a and b. Figure 2a indicates that the speed of demulsification depends on the nature of vegetable oils. If Vse, Vso, Vc, Vg, Vp are the speed (mV min⁻¹) of demulsification of emulsifier/sesame oil, emulsifier/soybean oil, emulsifier/groundnut oil and emulsifier/palm oil, respectively they increase in the following order: Vse (1.109), Vso (3.35), Vc (5.07), Vg (7.7), Vp (12.45). The correlation coefficients are 0.993; 0.986; 0.984; 0.988; 0.987, respectively with R² of 98.63; 97.39; 96.83; 97.63; 97.46. The demulsification speed of sesame oil is the lowest and the demulsification speed of palm oil is the highest.

Figure 2a shows that for emulsifier: oil ratio of 3:7, emulsion of sesame oil is more stable (lowest demulsification speed) whereas, palm oil forms a less stable emulsion among the oils studied (highest demulsification speed). Figure 2b that represents the same data as in Fig. 2a, after application of a logarithmic transformation permits the determination of the time for total

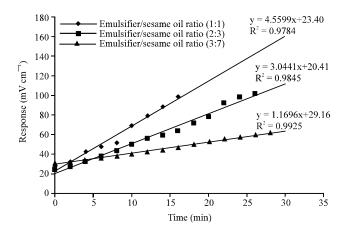


Fig. 1: Effect of the emulsifier/oil ratio on the sesame oil emulsion stability

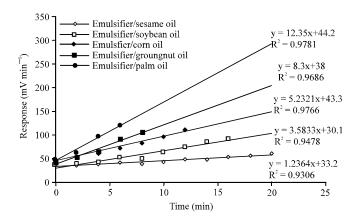


Fig. 2a: Effect of the nature of vegetable oils on the emulsion stability. (emulsifier/oil ratio 3:7)

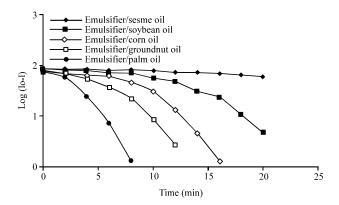


Fig. 2b: Determination of demulsification time according to the vegetable oil nature

demulsification that is equal to the intersection of each curve with the time axis. Figure 2b represents the curves of $\log (I_0\text{-}I)$, where I_0 is the response of pure oil or emulsifier because both are transparent to infrared rays emitted by the transphotometer and I is the response of the emulsion. Then the time of total demulsification of these emulsions in the experimental conditions are 8, 13, 16, 23 and more than 60 min, respectively for emulsions of palm oil, groundnut oil, corn oil, soybean oil and sesame oil.

Effect of the oil adulteration on the emulsion stability: Figure 3a, b and c present the results of the effect of the oil adulteration on the emulsion stability. The sesame oil adulterated with groundnut oil, soybean oil and palm oil, respectively, in the proportions ranging from 10 to 50% was used. As can be seen on these curves, the time or speed of demulsification depends on the adulteration rate. Figure 3a shows the variation of emulsion stability of sesame oil adulterated with groundnut oil at the adulteration rates ranging from 10 to 50%. If Tg, Tse, Tse 90, Tse 80, Tse 50 are the time of demulsification of pure groundnut oil, pure sesame oil, sesame oil adulterated with 10% groundnut oil, sesame oil adulterated with 50% groundnut oil, respectively, the time of total demulsification increases in the following way: Tse 50<Tse 80<Tg<Tse 90<Tse. Adulteration of sesame oil even at 10% with groundnut oil is perceived by means of emulsion stability.

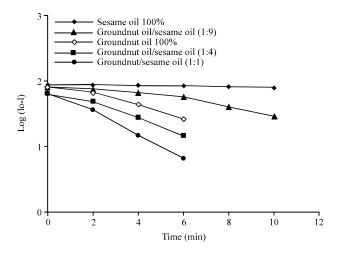


Fig. 3a: Effect of the groundnut oil adulteration on the sesame oil emulsion stability

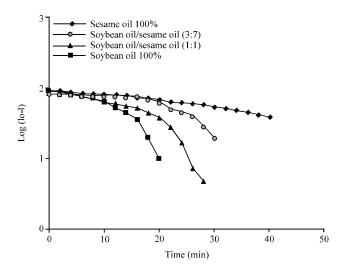
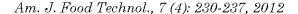


Fig. 3b: Effect of the soybean oil adulteration on the sesame oil emulsion stability

Figure 3b shows the variation of emulsion stability of sesame oil adulterated with soybean oil at the adulteration rates of 30 and 50%. If Tso, Tse, Tse 70, Tse 50 are time of total demulsification of pure soybean oil, sesame oil adulterated with 30% soy bean oil, sesame oil adulterated with 50% soybean oil, the total demulsification time increases as follows: Tso<Tse 50<Tse 70<Tse. Adulteration of sesame oil by soybean oil can be shown by the study of emulsion stability with the emulsifier used.

Figure 3c shows the variation of emulsion stability of sesame oil adulterated with palm oil at the adulteration rates of 50%. If Tpa, Tse, Tse 50, are the time of demulsification of pure palm oil, sesame oil, sesame oil adulterated with 50% palm oil, the total demulsification time increases as follow Tpa<Tse 50<Tse. This adulteration of sesame oil by palm oil was studied in order to confirm the rule because falsification of sesame oil could not be done with palm oil because the colour of palm oil is completely different of that of sesame oil.



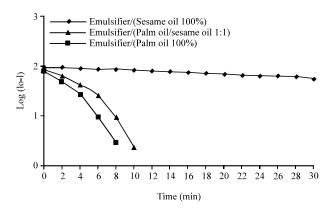


Fig. 3c: Effect of the palm oil adulteration on the sesame oil emulsion stability

DISCUSSION

Figure 2a clearly demonstrates that by means of the emulsion stability in the experimental conditions the five studied oils could be better identified than by means of refractive index, saponification index or iodine index used previously by Gunstone et al. (1986) because of large interference zone of these indexes. Adulteration of sesame oil with groundnut oil (Fig. 3a) or soybean oil (Fig. 3b) and even with palm oil (Fig. 3c) is easily detectable by means of speed of demulsification, or by time of the total demulsification of adulterated oil. Whether the speed or time of demulsification, all these parameters vary significantly even for an adulteration rate of 10% (Fig. 3a). Former studies will be done with adulterated oils ranging from 1 to 10% before comparing the performance of the method with electronic nose method (Gardner and Bartlett, 1994). It is therefore, possible to identify unequivocally studied vegetable oils by the transphotometry method presented. Among the five studied oils, sesame oil forms the more stable emulsion with nitromethane as emulsifier in all emulsifier/oil ratios. This study confirms the importance of the emulsifier/oil ratio on the stability of an emulsion (Fig. 1). The amount and the nature of emulsifier can facilitate the characterisation of certain liquids, by means of the speed or the time of total demulsification of emulsions formed.

The results obtained open a new field of research in the use of intermolecular forces, superficial and interfacial tensions, viscosity for the analysis and identification of liquid substances by the study of emulsion stability formed in the presence of a specific emulsifier or simply in the presence of an impurity. The work has to continue in physical characterisation of the dispersed media and in the case of vegetable oils not only for screening of falsification but also for standardisation of production as we obtain more and more vegetable oils of best quality by complementation processes.

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