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Review Article

PHYSICO-CHEMICAL PROPERTIES ANALYSIS BASED APPROACHES TO ASCERTAIN THE PURITY OF GHEE-A MINI REVIEW

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Ghee, the pure clarified fat derived solely from milk or curd or from desi (cooking) butter or from cream to which no coloring matter or preservative has been added. Ghee has an integral relation with Indian social and culinary culture. Ghee is one of the premium edible fat and it has so many health benefit. Demand of ghee is increasing day by day but due to supply gap especially in lean season the producers or the middle-men involved in the ghee trade, tend to adulterate ghee with cheaper oils and fats like vegetable oils, animal body fats, hydrogenated fats and sometimes even the non-edible mineral oils. Recently, the problem of adulteration has assumed a very serious dimension. Such a situation has damage the image of dairy industry. Methods presently adopted by food law enforcing agencies to ensure the quality of ghee are mainly based on the physico-chemical analysis of ghee. In this review all physico-chemical analysis based approaches have been discussed in this review.

Introduction

India is the largest producer of milk in the world, producing 146.3 million metric tons (MMT) in the year 2014-15 [1]. In India, Ghee is the second largest dairy product prepared from milk [2]. According to FSSR [3] **"Ghee"** means the pure clarified fat derived solely from milk or curd or from desi (cooking) butter or from cream to which no coloring matter or preservative has been added. Ghee performs a major and essential function as carrier of four fat-soluble vitamins viz., A, D, E, K and essential fatty-acids such as linolenic acid and arachidonic acid, apart from having rich and pleasant sensory attributes. The producers or the middle-men involved in the ghee trade, tend to adulterate ghee with cheaper oils and fats like vegetable oils, animal body fats, hydrogenated fats and sometimes even the non-edible

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mineral oils, especially during lean season to earn more money. Recently, the problem of adulteration has assumed a very serious dimension. Reports have been appearing in the print and electronic media, indicating the rampant malpractices of ghee adulteration particularly in the central and northern parts of the country. It is not known as to what extent these types of malpractices of adulteration are prevailing in the ghee trade in our country and what quality of ghee is available to the consumers. In order to ensure a genuine product to the consumer, the Government of India has prescribed the compositional standards for ghee, under FSSR [3] and AGMARK rules [4]. In this review we have go through various methods based on physical properties of fat as well as well as physico chemicals parameters analysis based approaches for detection of adulteration in ghee.

1- Methods based on physical properties

Physical properties of oils and fats are important criteria for judging their quality and have also been used to determine their authenticity.

Several methods, which were used to check the authenticity of ghee on the basis of physical properties, are as follows:

1.a Opacity Test

Singhal [5] developed an opacity test to detect the adulteration of ghee with animal body fats. He concluded that the adulteration with buffalo, goat and sheep body fats at 5 percent level and above could be safely detected by opacity test. However, the limitations of this test are that the detection of pig body fat up to 10 percent level is difficult and ghee from cotton tract area also cannot be distinguished. Test also failed to detect the body fats in ghee in the presence of vegetable oils [6].

Sharma and Singhal [7] carried out the opacity test at 25°C for pure fats (ghee, body fats and vanaspati) and adulterated ghee samples (5, 10 and 20% level) and observed almost the similar results as reported earlier by Singhal, [5]. Their study revealed that ghee took more than 35 min to become opaque, while vanaspati and lard (pig body fat) took 2 to 2.5 min and 6 to 7 min, respectively. On the other hand, tallow (buffalo and goat body fats) took very less time (<18 seconds) to become opaque. They did not find any significant difference in the opacity time of pure ghee and ghee samples adulterated with vanaspati and lard even up to 20 percent level.

1.b Critical Temperature of Dissolution (CTD)

Critical temperature of dissolution (temperature at which turbidity appears on gradual cooling of the fat dissolved in a warm solvent or solvent mixture) is a characteristic of a particular fat

which depends upon the nature of the solvent, nature and amount of most insoluble glycerides (usually tri- saturated glycerides) present in a fat as well as the mutual solubilizing power exerted on these glycerides by the soluble glycerides [8]. Bhide and Kane [9] observed the CTD values for ghee and vanaspati in the range of 39 to 45°C and 62 to 72°C, respectively, employing a 2:1 (v/v) mixture of 95 percent ethanol and iso-amyl alcohol, and reported that gross adulteration of ghee with vanaspati could easily be detected.

Kumar [10] & Upadhyay [11] reported that CTD value (^{o}C) for pure cow ghee ranged from 51.6 to 54.6 with an average of 53.3, whereas that for pure buffalo ghee ranged from 52.4 to 56.2 with an average of 54.3. Kumar [10] further reported that adulteration of cow as well as buffalo ghee with vegetable oil (soybean oil) and animal body fat (buffalo body fat) individually at 5, 10 and 15 percent levels and in their combinations at 5+5 (10), 10+10 (20) and 15+15 (30) % levels increased the CTD value and this increase was dependent upon the amount of adulterants added to the pure cow and buffalo ghee. Higher the level of adulterant added, greater was the increase in the CTD value of ghee samples. The author also reported that addition of animal body fat (buffalo body fat) caused slightly higher increase in the CTD value of ghee as compared to vegetable oil (soybean oil). Upadhyay [11] also reported that using CTD value only 15% adulteration could be detected.

1.c Fractionation of milk fat

Fractionation is a thermally controlled process (with or without solvent) in which the milk fat is subjected to a specific temperature/time profile to allow a portion of milk fat to crystallize. The crystals are then physically separated from the liquid fraction using vacuum filtration, pressure filtration, centrifugation etc. Single step melt crystallization or dry fractionation of milk fat into lower and higher melting fractions reveal that the lower melting fractions of milk fat contain somewhat greater levels of unsaturated acids and the fat constants for these fractions show a lower saponification number, a higher iodine value, a higher refractive index, and, of course, a much lower melting range [12].

Panda and Bindal [13] studied the crystallization behavior at 17°C of fat dissolved in a solvent mixture of acetone and benzene (3.5:1) and reported that ghee, ghee adulterated with body fats (10%) and ghee adulterated with vegetable oils and fats (10% level) took 19 min, 3 to 15 min and 22 to 23 min to crystallize. They concluded from the study that even low level adulteration of animal body fats and vegetable oils and fats could be detected in ghee. However, for cotton tract ghee, Panda and Bindal [13] carried out crystallization test at 25°C

instead of 17°C. But, the test could not distinguish between cotton tract ghee and the ghee adulterated with cow body fat at 5 percent level.

Upadhyay [11] reported that solvent fractionation method coupling with BR was very efficient for detection of body fat in both cow and buffalo ghee @20% level but less than 20% level could not be detected in this above said method. In same study the author carried out dry fractionation at temperature combination of 15ºC for 70-80 minutes followed by temperature time combination of 10ºC for 50-60 minutes to get first solid fraction and last liquid fraction of pure and adulterated ghee and suggested that BR reading of last liquid fraction even 10% level of body fat adulteration could be detected.

2. Tests Based on Physico-Chemical Constants

Certain well-known physical and chemical constants have been derived for the purpose of characterization of oils and fats. Among those constants three determinations, the Reichert-Meissl value, the Polenske value and the Iodine value, measure certain specific constituents of milk fat while other two, the Saponification value and Butyro-refractometer reading, give an overall average nature of the constituent fatty acids present [14]. These physico-chemical constants are described briefly in the following sections:

2.a Butyro Refractometer Reading (BR)

The values for B.R. readings of milk fat (40-45) and vegetable oils and fats (above 50) are so wide apart [5,15]. Feeding of cottonseed oil raises the B.R. reading by 5 units in case of ghee [14,16]. Normally, BR reading or refractive index of oils and fats increases with the increase in unsaturation and also chain length of fatty acids. The B.R. readings of animal body fats are in the range of 44 to 51 [5]. Adulteration of milk fat with animal body fats and vanaspati [17] at a level of 5 to 20 percent increased its B.R. readings. Arora *et al.*[`18] have developed a simple platform test for the detection of vegetable oil (refined mustard oil) added to milk at a level higher than 10 percent of the original fat on the basis of increase in B.R. reading of the fat.

Patel [19] reported that vegetable oil added to cow ghee at 10 percent level and above levels could easily detected by B.R reading, Whereas, in buffalo ghee, only 15 percent level of vegetable oil could be detected. On the other hand animal body fat added to both types of ghee (cow and buffalo) could not be detected less than 15% level. Pranoti [20] reported that using B.R reading 20% lard could be detected in cow ghee but this said method was not useful to detect lard adulteration in cow or mix ghee. Kumar [10] reported that B.R. reading could not be used to detect body fat adulteration in ghee (cow or buffalo) less than 15% level.

2.b Reichert-Meissl *(*RM)value

RM value is the number of millilitre of 0.1 N alkali solution required to neutralize the steam volatile, water soluble fatty acids distilled from 5 g of fat under specified conditions. This constant for milk fat is quite significant since it is primarily a measure of butyric ($C_{4:0}$) and caproic ($C_{6:0}$) acid. RM value for milk fat ranges from 17 to 35, which is well above the value (generally 1) for all other fats and oils except coconut oil and palm kernel oil for which the value ranges between 4 to 8 [5]. Feeding of cottonseed to milch animals lowers the RM value of ghee by 5 to 6 units [14].

Patel [19] reported that RM-value was higher in buffalo ghee as compare to cow ghee. The author also reported Vegetable oils and animal body fats showed negligible RM values as against high RM values observed for cow and buffalo ghee and by using this technique higher than 10% level of vegetable oil adulteration could be detected in ghee.

Pranoti [20] reported that pure cow adulterated with body fat 10% level and pure buffalo ghee body fat adulteration 20% level could be detected by RM-value analysis.

Rakesh [21] studied that adulteration of pure cow ghee with soybean oil at 5% level or above, whereas animal body fats individually at 10% or above could be detected by using RM value. The adulteration of buffalo ghee with all the adulterants individually at 20% level or above could be detected by using RM value.

2.c Polenskevalue

Polenske value denotes the number of millilitre of 0.1 N alkali solution required to neutralize the steam volatile and water insoluble fatty acids distilled from 5 g of fat under specified conditions. This value is substantially a measure of caprylic ($C_{8:0}$) and capric ($C_{10:0}$) acid. The Polenske value for milk fat ranges from 1.2 to 2.4. This value for other oils and fats [5,16] is also low (less than 1) except the coconut oil (15-20) and palm kernel oil (6-12). Feeding of cottonseeds to milch animals reduces the Polenske value of ghee by 0.3 to 0.7 units [14]. Patel (2011) reported that Polenske value overall range was 1.30 to 1.80 for both pure cow and buffalo ghee and when ghee added with more than 15% body fat the range deviated to 1.28 as compare to normal range. In another study Pranoti [19] reported that Polenske value was not suitable to detect adulteration in ghee with body fat at any level. Same type of observation was recorded by Rakesh [21], who reported that Polenske value could not be used to detect upto 20% level of adulteration in ghee.

2.d Iodinevalue

Number of grams of iodine absorbed by 100 g of fat under specified conditions represents the iodine value. This constant is a measure of unsaturated linkages present in a fat. The iodine value for milk fat ranges from 26 to 35, which is low in comparison to most of the other fats & oils [22]. Animal body fats show slightly higher iodine value ranging from 36 to 49. Whereas, for vegetable oils, the value is very high (74-145) except coconut oil (6-10) and palm kernel oil (10-18). For hydrogenated fats, it lies in the range of 70 to 79. Feeding of cottonseed raises the iodine value of ghee up to 10 units [14]. Upadhyay [20] studied that using iodine value 15% ground nut oil could be detected in buffalo ghee whereas 5% ground nut oil could be detected in cow ghee. In another study Gandhi *et al*. [12] reported that solvent fractionation couple with iodine value analysis of liquid fraction able to detect 30% level of sheep body fat in ghee.

2.e Saponificationvalue

Saponification value which denotes the number of milligrams of KOH required to saponify one gram of fat gives an indication of average molecular weight of fatty acids present. For milk fat, animal body fats, vegetable oils and hydrogenated fats, the value ranges from 210 to 233, 192 to 203, 170 to 197 and 197 to 199, respectively. Coconut oil and palm kernel oil show higher saponification value ranging from 243 to 262 [5]. Feeding of cottonseeds to milch animals lowers this value by 7 units [14]. Liquid portion of ghee separated on storage at 30 to 35°C for one month showed higher saponification value than solid portion [22].

Several earlier workers [5] have reported that physico-chemical constants failed to detect the adulteration of milk fat with beef tallow, refined cottonseed oil, hydrogenated oils and even coconut oil separately or in mixture even up to 10 percent level. Singhal [5] also employed the physico-chemical constants for detecting the animal body fats (buffalo, goat, sheep and pig) added to buffalo and cow ghee and reported that the values for Reichert-Meissl, Polenske, and BR indices remained within the legal limits for normal ghee, when adulterated with animal body fats at 20 percent level. However, when adulteration was done at 50 percent level, the values remained within the legal limits set for cotton tract ghee. Sharma and Singhal [24] also confirmed the above findings using body fats (buffalo, goat and pig) and vanaspati ghee irrespective of mode of adulteration whether added directly to ghee or through milk.

Conclusion

Ghee is a one of the costliest edible fat consumed allover India Therefore it is highly prone to adulteration with cheaper oils/fats. The problem of adulteration has assumed a very serious dimension, by adulterating ghee with cheaper oils and fat the unscrupulous traders are not only robbing the people of their money, but also playing with the cultural sentiments of people, besides adversely affecting their health. Several methods based on the physico-chemical characteristics of oils and fats have been developed to detect the various types of adulterant fats such as animal body fats and vegetable oils in milk fat, but most of the methods are quite tedious and time consuming. So researchers are always in-search of rapid methods that can solve this problem very quickly.

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