

GC Fingerprint Method to Investigate Adulteration of Coconut Oil with Palm Oil

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ABSTRACT: Coconut oil is the commonly used edible oil in Sri Lanka. Due to similar chemical and physical characteristics, palm oil is a good candidate to adulterate coconut oil targeting profit gains while ignoring the health impacts. In this study a gas chromatographic method was developed to investigate the levels of adulteration. The developed method revealed that 60% of the tested coconut oil samples purchased from Colombo Municipality area is adulterated with palm oil. The level of adulteration varied from 6 to 77% with four of them having over 50% adulteration levels. The results are verified using statistical analysis technique.

KEYWORDS: Coconut oil, Adulteration, Fatty acid methyl ester.

I. INTRODUCTION

Coconut oil is an edible oil that has been used in most of the countries for a long period of times. Coconut oil is produced using dried kernel, which contains about 60-65% of the oil. The coconut oil contains 92 % of saturated fatty acids, and 70% of them are lower chain saturated fatty acids to medium chain fatty acids. These are present in the form of triglycerides.

Adulteration of consumer products by inferior materials for economic gains is well-known phenomenon in food industry. The choice of the adulterant is based on the financial gains, easy blending ability, availability and the similarity of the chemical and physical properties of the oil to the adulterant. Among the common adulterants for coconut oil, palm oil seems to be the widely available choice.

The palm oil contains saturated fatty acids, mainly palmitic acid. It is a semi solid at room temperature but in warmer climates it is a liquid. Palm oil contains saturated and unsaturated fats in the form of glyceryl laurate.

Palmitic acid, which in turn have been associated with increased risk of coronary heart disease and some tumours. However, more recent investigations on the topic seem to have reconsidered the negative role of the dietary saturated fatty acids (SFAs) as a risk factor for cardiovascular diseases and show that not only the type of fat, but also that the triglyceride structure plays a role in cholesterolaemia [1]. As regards to a role in cancer, specific studies on dietary palmitic acid or palm oil and the risk of cancer development are scanty, and the evidence is not convincing [1].

According to the World Health Organization report in 2003, palmitic oil consumption contributes to an increased risk of developing of cardiovascular diseases [2]. The palm oil contains long chain fatty acids compared to coconut oil and they are absorbed to the body. In 2003 Dutch scientist found that the ratio of total cholesterol to high density lipoproteins (HDL) cholesterol is the best indicator of heart diseases risk [2]. Palmitic acid is responsible for increased the total: HDL cholesterol ratio. It is comparing to higher than lauric acids and myristic acid, which are present in palm kernel oil and coconut oil. Palm oil increases the total: HDL cholesterol ratio more than the average. Therefore, palm oil is harmful than coconut oil for blood cholesterol level [2].

Additionally, oxidized palm oil induces reproductive toxicity and organotoxicity particularly of the kidneys, lungs, liver and heart [3].

The application of the research is to determine the quality of coconut oil and identify the adulteration of coconut oil with palm oil. The method is based on lauric and palmitic fatty acids present in different oil types. The analytical parameter of log (area of lauric/area of palmitic) were evaluated based on linear regressions to establish quantitative measures for the present of adulterant levels. These linear regressions were exploited to assess the levels of adulteration for twenty commercial coconut oil samples purchased from Colombo Municipal Area.

II. RELATED WORK

Having similar chemical properties, the coconut oil and the adulterant cannot be distinguished easily leading to complications in identification and quantification of the adulterants.

Several techniques have been developed to detect coconut oil adulteration with other edible oil which include refractive index method [4], FTIR spectroscopy method [5], [6], [7], [8], [9], high performance liquid chromatography [10], thin layer chromatography and colorimetric method [11] and FTNIR [12], [13], method.

The refractive index method is already used to determine the percentage of adulteration of coconut oil with palm oil. It was identified that the maximum adulteration percentage of coconut oil is 30% [4]. The refractive index method is a simple laboratory measurement technique but, it is not a confirmation test. The results are variable frequently when measured from the Abbe's refractometer. Further RI value is also depending on the temperature. Hence, it is difficult to develop an acceptable analytical parameter to assess the level of adulteration with sufficient accuracy and precision. In food analysis, chromatographic based methods are reliable and more sensitive than the classical methods.

The FTIR spectroscopy is another technique which is used to detect the adulteration of coconut oil with palm oil [5]. This technique offers fast and reliable detection of adulterations. The measurements of FTIR method were made on pure virgin coconut oil as well as coconut oil adulterated with palm oil only from 0.5–50% w/w [5].

High performance liquid chromatography [10], thin layer chromatography and colorimetric methods [11] are often time consuming and hence may not be adoptable to handle large number of consumer samples originated and distributed from different origins.

Several FTIR and NIR based methods have documented for assessing the adulteration of edible oils [6], [7], [8], [9], [12], [13], but not for the investigation of palm oil in coconut oil.

The developed Gas chromatography technique is consistent and reproducible. The method was used to determine the concentration of palm oil from 0 to 100 % w/w in coconut oil. The GC method includes simple pre sample preparation procedure with maximum time of 5 minutes. Therefore, GC technique is user friendly, less cumbersome and rapid than the above techniques and it is ideal in assessing the quality of the coconut oils.

III. METHODOLOGY

Pure coconut oil and pure palm oil were selected as the controls and the synthetic mixtures were prepared by mixing them with appropriate proportions. A series of blended oil samples were prepared having the final composition of 0 to 100% of palm oil in coconut oil. Gas chromatographic analyses were carried out for pure coconut oil, pure palm oil, standard series of oil mixtures and commercially available oil samples according to the AOCS Official Methods [14]. The Gas chromatography (GC -14B, SHIMADZU) was used for the analysis and the effluents were monitored using a flame ionization detector. The injector temperature was set at 250 °C. A 30 m Omegawax™ 320 capillary column was with 0.3 mm outside diameter and 0.25µm of film thickness was used for the separation. The



temperature program commenced at 100 °C, held for 4 min, ramped at a rate: 6°C/min to 240 °C and held at 240 °C for 10 min.

The oil was introduced in to the 50 ml reaction flask. 6 ml of 0.5 M methanolic- NaOH and refluxed until the oil globules go into solution. This step was carried out 5-10 min. Then 7 ml BF₃-methanol reagent was added through the condenser and boiled for 2 min. A portion of 10 ml of heptane was added through the condenser and boiled for 1 min longer. To the refluxed sample 15 ml of saturated sodium chloride solution was added and shaken vigorously for 15 sec while the solution is still trepid. Then sufficient saturated NaCl solution was added to float the heptane solution of the methyl esters into the neck of the flask. About 1ml of heptane layer was transferred into a test tube and a small amount of anhydrous sodium sulphate was added. The dry heptane solution was injected directly in a gas chromatography. This procedure was followed for pure coconut oil, pure palm oil, standard series of oil mixtures and commercially available oil samples. A similar procedure was followed for the preparation of methyl esters from fatty acids. Commercially available coconut oil samples were collected from distribution centres in Colombo Municipality area and its suburbs for assessing the level of adulteration.

Statistical analysis of results

A blind sample was analysed twenty times using same instruments by GC method and classical Iodine value method. The multiple analysis test at different levels were carried out for known concentration of sample series (1 to 80%) to calculate the accuracy of the test method at different adulteration levels.

IV. EXPERIMENTAL RESULTS

The control samples are identified as pure using classical test results of refractive index values, free fatty acid values, saponification values and iodine values. The results are summarized in Table I.

Table I: Classical test results of control coconut oil and palm oil and standard values for edible coconut oil and edible palm oil

Parameter	Control coconut oil	Control palm oil	Standard value for edible coconut oil	Standard value for edible palm oil
Refractive index at 40 °C	1.4485	1.4560	1.4485 – 1.4492	1.4546 – 1.4560
Free fatty acid	0.88% as lauric	0.08% as palmitic	≤ 1.0% as lauric	≤ 0.1% as palmitic
Saponification value	251	200	Not less than 245	195 – 205
Iodine value	8	52	7 – 10	50 – 55

Instrumental Analysis

The chromatographic fingerprints of coconut and palm oils were found to be similar. However, the relative abundance of the signals exhibits a significant difference between the two types of oils. Since the common signals were present in both the oils (Figure1 & 2), different combinations of signal responses were evaluated to find a correlation for the blended series. The best correlation was found between log (area of lauric / area of palmitic) and the composition of palm oil as shown in Figure 3. The correlation coefficient was found to be 0.99.

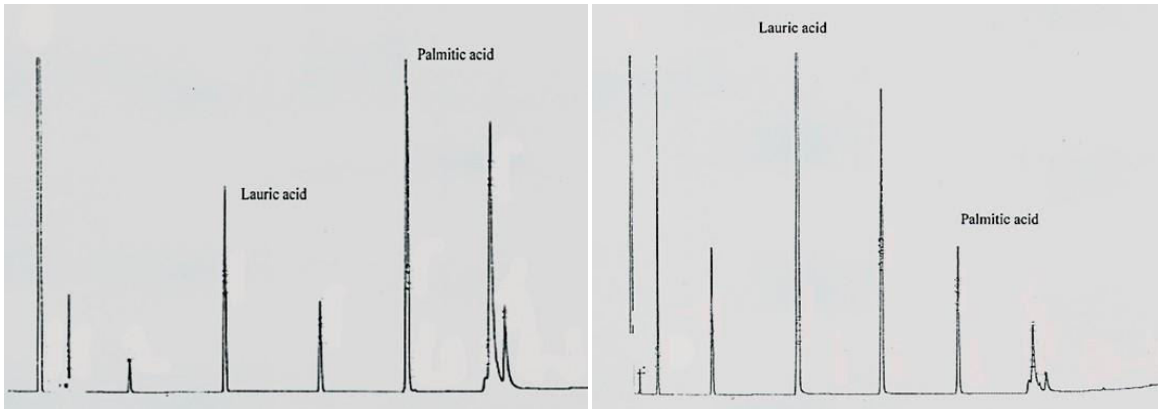


Fig 2: GC Fingerprint of pure palm oil

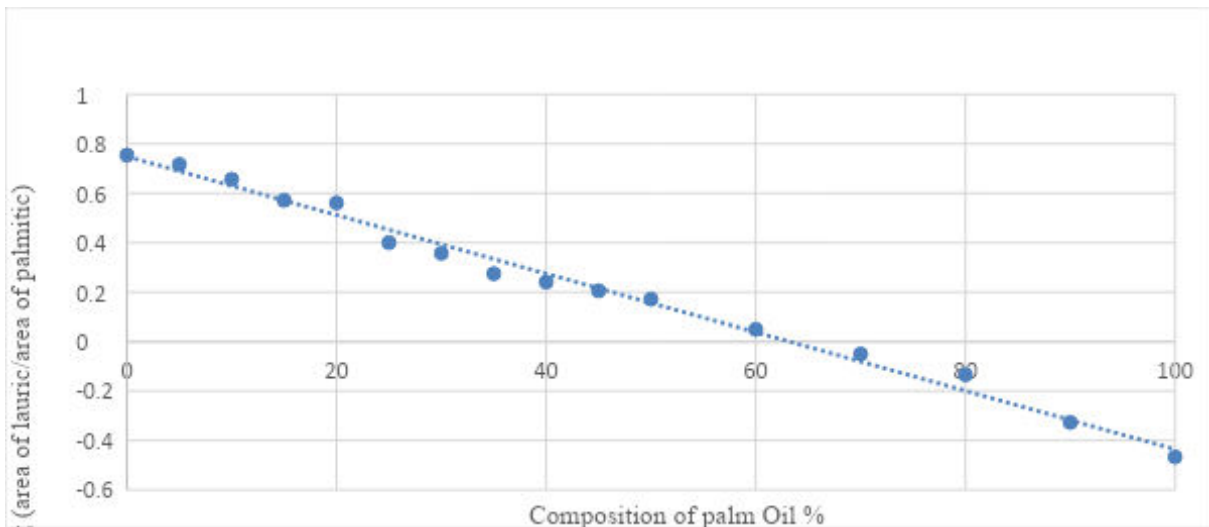


Fig 3: Correlation between log (area of lauric / area of palmitic) and composition of palm oil for blended mixtures

According to the relationship between log (area of lauric/area of palmitic) value and composition of palm oil %, it can be observed that when the amount of palm oil in the oil mixture is increased, the log (area of lauric/area of palmitic) value decreased. This correlation was used to determine the level of adulteration of coconut oil with palm oil in the test samples.

The results obtained from GC method and classical method (Iodine value method) are used to validate the test method and results are summarized in Table II.



Table II: Palm oil composition from GC method and Iodine value method for the blind sample

Detected palm oil composition from Iodine value method %		Detected palm oil composition from GC method %	
	22.56		19.25
	20.87		21.69
	22.35		20.12
	22.65		20.23
	20.46		21.03
	22.51		20.56
	20.53		20.48
	19.89		20.57
	21.64		20.32
	20.58		21.89
	22.31		21.35
	20.85		22.35
	19.98		19.65
	21.12		20.64
	20.56		20.66
	19.92		22.54
	20.54		20.45
	21.89		19.86
	20.22		21.52
	20.35		20.32
Mean	21.14	Mean	20.77
Standard deviation	1.07	Standard deviation	0.87

Blind sample having 23% palm oil resulted similar results from both the methods where GC method is more reproducible with a lesser standard deviation compared to classical method and classical method is somewhat accurate compared to GC method. But GC method is fast and user friendly method compared to iodine value method which uses corrosive chemicals. Hypothesis was generated to validate the result at 95% confidence interval. The t- statistic distribution analysis proves that $t_{crit} > t_{cal}$. The mean value of two different methods (null hypothesis) are not significant.

The Accuracy of the test method is calculated from results obtained from GC method for known concentration series (1% to 80%) of palm oil in coconut oil. The results are shown in Figure 4.

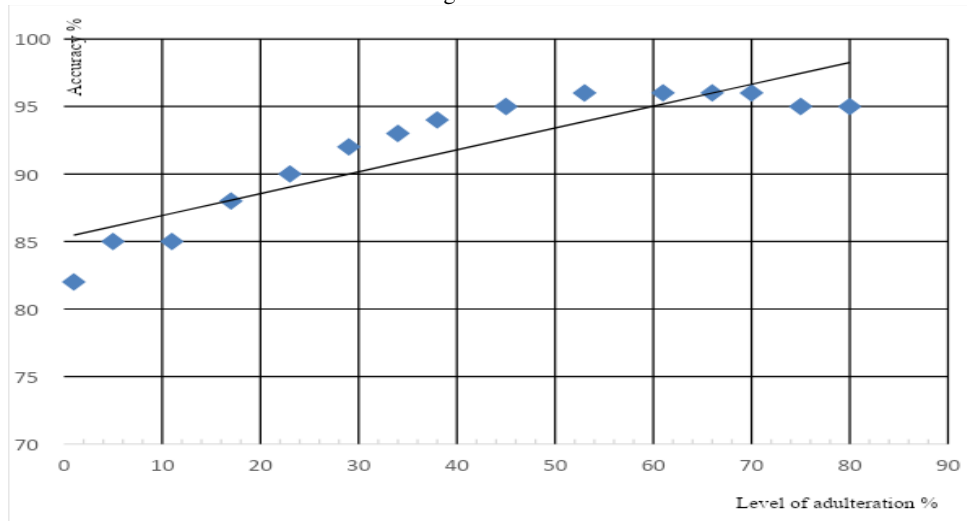


Fig 4: Accuracy of GC method at different adulteration levels

According to the graph of accuracy vs. level of adulteration the accuracy is better than 80% for all the level of adulteration from 1 to 80%. Accuracy improves to 90 % or better when the adulteration level is above 20%. Since higher adulterations are more economical, developed method is more reliable in assessing the commercial samples.

Assessing 20 different commercially available coconut oil in the Colombo Municipality are summarized in Table III.

Table III: Level of adulteration for the commercial samples

Sample No	Area of lauric (L)	Area of palmitic (P)	Log (L/P)	Estimated level of adulteration
1	617982	172953	0.5530	16% Adulterated
2	651561	108953	0.7767	Less than 1%
3	584452	164621	0.5503	17% Adulterated
4	465837	78464	0.7736	Less than 1%
5	306132	39386	0.8906	Less than 1%
6	661591	161386	0.6127	11% Adulterated
7	567333	203217	0.4459	25% Adulterated
8	471709	331853	0.1527	50% Adulterated
9	504792	93079	0.7343	1% Adulterated
10	587435	223516	0.4197	28% Adulterated
11	566246	100003	0.7530	Less than 1%
12	481925	116048	0.6183	11% Adulterated
13	417989	86859	0.6824	6% Adulterated
14	569323	93386	0.7851	Less than 1%
15	546916	93991	0.7648	Less than 1%
16	204380	78675	0.4146	28% Adulterated
17	427481	327302	0.1160	53% Adulterated
18	603201	113611	0.7250	2% Adulterated
19	191372	239943	-0.0982	71% Adulterated
20	259573	381559	-0.1673	77% Adulterated

Out of the twenty coconut oil samples, eight samples had the adulteration levels of less than 5% which can be considered as unadulterated. Four samples had significantly higher levels of adulteration at 50 %, 53 %, 71% and 77% respectively. These findings are comparable to the adulteration levels in the region where 50 % of palm oil was found in virgin coconut oil samples sold in Kerala, India [5].

V. CONCLUSION

A reliable analytical method was developed to assess the level of adulteration of coconut oil by low cost palm oil. The percentage of adulteration of these oils has been deduced by using the gas chromatographic technique. This method allows determining palm oil adulteration to coconut oil. This reveals that GC method can also be used as a quality control technique for finding the adulteration of coconut oil. From this study, it has been observed that in coconut oil is adulterated by palm oil up to 77%. But the method is more accurate for higher level of adulteration in coconut oil.

However, it cannot be concluded that palm oil is the only adulterant in the commercial coconut oil samples. Any other oil may have been used for adulteration. This problem arises because the quantifications were based on the intensities of the signals that are dominated by palm oil and coconut oil. Hence, the method assesses the level of adulteration but it does not identify the type of adulterant.

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