A Brief Review on trans fatty acids in partially hydrogenated vegitable oil[30]; A Organic Chemical

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Abstract

The FA composition and trans FA (TFA) level of various hydrogenated vegetable oils and blended fats sold in Pakistan are presented in this study[5]. The researchers looked at 34 vanaspati (vegetable ghee), 11 shortenings, and 11 margarines. Saturated FA, cis monounsaturated FA, and cis PUFA[5] content ranged from 27.8–49.5, 22.2–27.5, 9.3–13.1 percent in vanaspati, 15.8–36.0, 2.7–7.0 percent in vegetable shortenings, and 2.9–20.5 percent in margarines, respectively. TFA levels in vanaspati samples were much higher, ranging from 14.2 to 34.3 percent. TFA amounts in shortenings ranged from 7.3 to 31.7 percent. TFA levels in hard-type margarines ranged from 1.6 to 23.1 percent, whereas TFA levels in soft margarines were less than 4.1 percent. Trans fatty acids (TFA) are created by hydrogenation of unsaturated oils or biohydrogenation in ruminant animals' stomachs[2]. TFA levels are high in Vanaspati ghee and margarine. TFA consumption has been linked to an elevated risk of cardiovascular disease in several studies (CVD)[24]. TFA raises the ratio of LDL cholesterol to HDL cholesterol, which increases the risk[4].

Keywords: trans fatty acid: vanaspati: elaidic acid: monounsaturated FA: cis PUFA, Margarine

Introduction

Fatty acid is a key component of lipids (fat-soluble components of living cells) in plants, animals, and microbes[8]. A fatty acid, in general, is made up of a straight chain with an even number of carbon atoms, hydrogen atoms running the length of the chain and at one end, and a carboxyl group (COOH) at the other end. It's because of the carboxyl group that it's an acid[7].

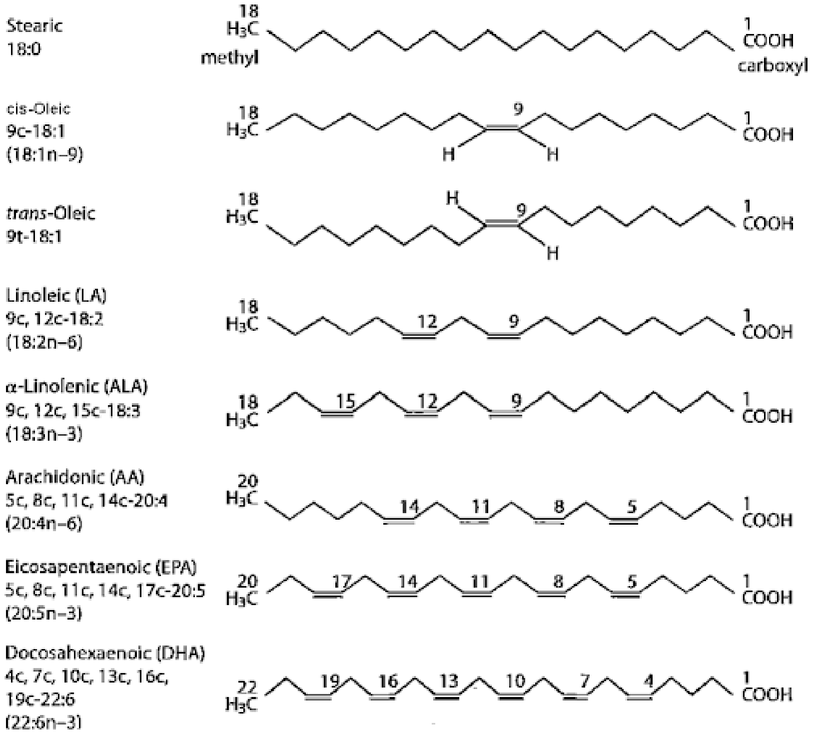
Saturated fatty acids are those that have no double bonds (have maximum number of H atoms)

Saturated fatty acids have a linear structure, come from animal sources (fats), and are solid at room temperatures[12].

Monounsaturated (one double bond) or polyunsaturated (more than one double bond) fatty acids have double bonds[8].

Unsaturated fatty acids have a bent structure, are derived from plants (i.e. oils), and are liquid at room temperature.

Fatty acids are the most common type of lipid in the human diet, and they are mostly found in nature as glycerol esters that form triacylglycerols. Fatty acids contain cis un saturations in both the plant and animal kingdoms. The hydrogens attached to the double bond carbons are on the same side in this configuration. The hydrogens are coupled to un saturations in another potential form, called trans. On opposite sides, there are carbons. Unsaturated fatty acids that have one or more un saturations. Trans fatty acids are fatty acids that have a trans configuration (TFA). Monounsaturated trans fatty acids (MTFA), a group of fatty acids with only one unsaturation, which must be in the trans form, are included in this category. Polyunsaturated trans fatty acids (PTFA) have two or more unsaturations, either entirely trans or not, like their cis counterparts (Dutton 1979, Wolff 1992). Concern about the ratio of TFA-rich foods consumed has developed in recent years, owing to the harmful effects of these lipids on plasma lipoproteins, which increase low density lipoprotein (LDL-c) and lipoprotein a(Lp[a]) levels while decreasing high density lipoprotein (HDL-c) levels (HDL-c). This condition contributes to a rise in the LDL-c/HDL-c ratio, which is a key predictor of the risk of cardiovascular disease development (Ascherio et al. 1999, Hunter 2005). Furthermore, excessive TFA consumption during pregnancy has been linked to consequences on intrauterine development (Decsi and Koletzko 1995). High intake of these fatty acids has also been linked to an increase in allergy disorders (Weiland et al. 1999). Based on these findings, it is recommended that dietary TFA levels be reduced. As a result, it's critical to think about TFA generating activities in foods, as well as alternatives for reducing them. The goal of this research is to discuss TFA production in vegetal oil refining and hydrogenation, meat irradiation, food frying, and bio hydrogenation from this perspective.



Hydrogenated Vegetable oil

Butter replacements were first produced in Europe in the mid-nineteenth century[10], primarily as a result of the high cost of butter. In 1869, a French chemist, Me ge Mouries[1], invented a passable butter substitute at Napoleon Bonaparte's request. This product, which is made composed of a small amount of bovine tallow[1], had a good consistency and melted in the mouth, which helped it gain customer appeal. Lard was also employed in the development of butter replacements in subsequent years (Ghotra et al. 2002).

Sabatier and Senderens, two French scientists, found in 1897 that the difference in consistency between vegetable oils and butter[1], as well as tallow and lard, was attributable to the lesser levels of hydrogen atoms present. This breakthrough was made possible because to the use of nickel as a catalyst, which enabled the invention of a method for producing fats from vegetable and marine oils (Gun stone 1998)[1].

In 1903, the hydrogenation technique was used to make lipids from sperm whale oil for the first time in industry in England. The procedure was first employed in 1909 to make tallow replacements, which were in short supply at the time and hampered soap manufacture (Johnson 1998). Hydrogenated fats and margarines made from cotton and soy oils began to be produced in Europe and the United States in the following years (Shurtleff and Aoyagi 2004)[1].

The hydrogenation business grew rapidly from the 1930s through the 1950s, owing to the widespread use of margarines and hydrogenated fats during[10] WWII (Shurtleff and Aoyagi 2004). Until 1940[1], however, margarine was thought to be a poor alternative for butter. The Food and Drug Administration (FDA) of the United States[25] produced a study in 1941 granting margarine the status of a basic food (Ghotra et al. 2002)[1].

Researchers from the Northern Regional Research Center in the United States discovered in the late 1950s that alpha-linoleic acid (18:3 9c, 12c, 15c) was linked to the creation of foul odours while frying meals in soy oil. As a result, it was proposed that selective hydrogenation be developed as an alternative to reduce the amount of this fatty acid in soybean oil (Gray and Russell 1979)[1]. This technique resulted in light hydrogenation, a procedure that lowered alpha-linoleic acid content in oil to 3% of total fatty acids and increased the possibility of synthesising fats with specified properties (Ackman and Mag 1998)[1].

The hydrogenation business first arose in Brazil in the 1950s, generating hydrogenated fat and hard margarine[10]. It began making soft margarine in 1970 by combining hydrogenated fats with variable melting points[1]. The development of selective hydrogenation improved the hydrogenation process, allowing for the generation of more and more specific fats and their growing application in food production[1]. As a result, animal fats were almost completely replaced in the Brazilian population's diet (Pelaez-Alvarez et al. 1991)[1].

The reaction of unsaturated fatty acids from either vegetable or marine oil in the presence of a catalyst, usually nickel, is the basis for hydrogenation[16]. The goal is to increase the oxidative stability of oils by[1] lowering their unsaturated fatty acid content and altering their physical properties, hence expanding their applicability.

The temperature of the oil, the hydrogen pressure[13], the stirring speed, the reaction time, and the catalyst type and concentration all play a role in hydrogenation. Hydrogenation is defined as partial or total[1], selective or nonselective, depending on the process circumstances (Gray and Russell 1979)[1].

Selectivity refers to the preferential hydrogenation of unsaturated fatty acids over saturated fatty acids, resulting in the least amount of saturated fatty acids feasible (Nawar 1996)[13]. Low hydrogen pressure, moderate stirring speed, and high temperatures are commonly used to achieve good selectivity[20]. As a result, there is a scarcity of hydrogen on the catalyst surface, favouring the creation of TFA (Ackman and Mag 1998)[23].

The hydrogenation industry has prioritised the manufacture of high TFA fats for decades, not only to reduce hydrogen consumption, but also to improve the physical, chemical, and organoleptic features of fats (Weiss 1983, Karabulut et al. 2003). Many catalysts were treated with HS, SO, CS, or CO to reduce the number of hydrogen adsorption sites and increase geometric polymerization (Allen 1981, Johnson 1998).

In the 1960s, researchers began to investigate the relationship between catalyst and hydrogenation selectivity, resulting to the discovery of various catalysts, including copper, nickel, palladium, and platinum (Gray and Russel 1979).

Copper-based catalysts have a high selectivity for alpha-linolenic and linoleic acids while forming low TFA. These catalysts were mostly utilised in light hydrogenation in the 1970s and 1980s. However, their application has been limited due to their poor activity and catalytic effect on unsaturated fatty acid oxidation (Ackman and Mag 1998).

As a result, nickel became the catalyst of choice because to its high activity, reasonable selectivity, filterability, reusability, decreased impact on unsaturated fatty acid oxidation, and lower cost when compared to palladium and platinum catalysts (Gray and Russel 1979, Okonek et al. 1995). Nickel is usually supported onto silica, aluminium, chromium, or cobalt oxides to boost its catalytic activity and make post-hydrogenation removal easier (Johnson 1998). Although there are various advantages to using nickel, hydrogenation is never completely selective, and TFA generation is high. Furthermore, reusing a catalyst reduces selectivity and increases TFA creation. (Gray and Russel 1979).

When compared to conventional catalysts in the production of fats with an iodine value equal to70, the development of modified nickel catalysts that allowed the hydrogenation process to be carried out at lower temperatures without significantly affecting reaction selectivity and with lower TFA formation has allowed for a reduction of up to 38.6% in TFA production during soybean oil hydrogenation. For iodine values of 90 and 60, TFA levels in canola oil and lipids dropped by up to 50.3 and 66.7 percent, respectively.

Noble metal catalysts, such as platinum and palladium, have strong catalytic activity, allowing for hydrogenation speeds comparable to nickel at low temperatures (Johnson 1998). Although this condition lowered TFA generation, the increased catalytic activity necessitates the use of lower catalyst concentrations, which necessitates an increase in filtration efficiency, limiting their utilisation (Gray and Russell 1979). Modified-platinum was one among these catalysts that allowed for very selective hydrogenation with less TFA production (Okonek et al. 1995).

Allen and Kiess (1955) hypothesised a mechanism for the production of geometric and positional isomers during hydrogenation based on the semi-hydrogenation/dehydrogenation sequence (Figure 1), which was later verified by other investigations (Allen and Kiess 1956, Allen 1981). According to the authors, a hydrogen atom can reach any end of a double bond during hydrogenation and generate a free-radical site, which is presumably bound to the catalyst. This free radical site is quite unstable, and if the catalyst is partially covered in hydrogen, a hydrogen atom adjacent to the carbon can be removed, regenerating the double bond or forming a positional isomer[1]. Because the development of a free radical site allows for unrestricted rotation, the resulting double bond can be cis or trans[1].

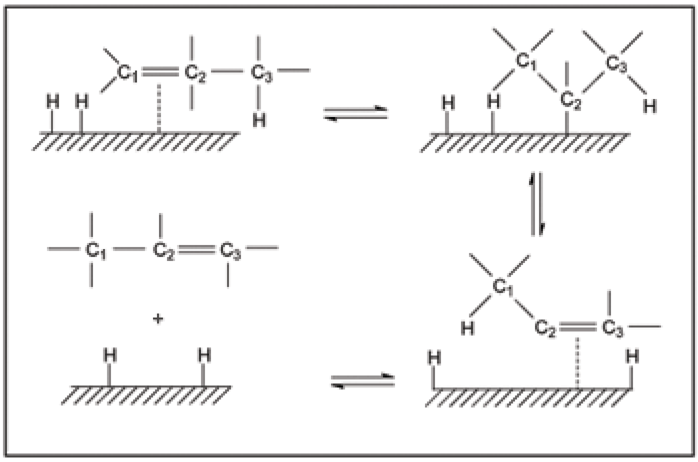


Fig. 1 – Mechanism of formation of geometric and positional isomers in the hydrogenation process (Min 2005).

Uses of trans fatty acids

Unsaturated fats derived from vegetable oils are known as trans fats. They're frequently used to make margarine and commercially baked or fried dishes[14]. Trans-fatty acids are synthetic fats that are formed during the hydrogenation process, which is used to preserve polyunsaturated oils from going rancid and to maintain them solid at room temperature. They may be especially harmful to heart health and may increase the risk of some malignancies[4].

Most commercially available fried and baked foods include transfat[31]. Trans-fat is found in cakes, frozen pizza, tortilla chips, cookies, crackers, biscuits, coffee creamer, and margarine. Reading the nutrition facts panel on a packaged item might reveal the amount or percentage of trans fat in that product[11].

The ability to undertake an in-depth assessment of diverse oils and fats products available throughout Pakistan[5] has been made possible by recent technological breakthroughs in measurements of positional and geometrical trans isomers by capillary GC[5]. The goal of this comprehensive investigation was to determine the FA content of a variety of locally sold hydrogenated vegetable oils, shortenings, and margarines, with a focus on TFA[5].

FSSAI limits for trans fatty acids

FSSAI has set a limit for industrial TFAs in edible oils and fats of not more than 3% effective January 1, 2021, and the limit would be further decreased in all fats and oils to not more than 2% by January 1, 2022, as per its 2018 plan. Food products containing more than 2%[26] industrial trans fatty acids will be prohibited beginning January 1, 2022. With the Food Safety and Standards Authority of India (FSSAI)[19] announcing a deadline of January 1, 2022 for restricting trans-fat levels in food items and edible oils and fats to 2%, India will join a group of over 40 countries working on policies to eliminate trans-fats from their food supply chains[27].

How to reduce TFA in food products?

TFA levels can be reduced by reformulating food products. Trans fat level was lowered to less than 0.5 gm per serving in 95 percent of grocery products and 80 percent of restaurant goods in the United States, for example[2]. Fat interesterification is a form of oil in which the fatty acids have been transferred from one triglyceride molecule to the next[2]. With the use of catalysts or the lipase enzyme, interesterification of vegetable oils can exchange an unsaturated fatty acid (such as oleic acid or linoleic acid) at the middle position (sn-2) of glycerol with a saturated fatty acid (stearic acid)[2]. The majority of long-term research found little evidence that interesterification of dietary fats alters lipoprotein composition[2]. More research is needed in this area, particularly on the effect of interesterified fat on inflammatory markers[2]. Genetically engineered fatty acids: Fatty acids with desirable qualities can be obtained by genetic engineering, and then the TFA content in food products can be lowered by reformulation[2].

Prepration of methyl ester

The transfat analysis method utilised in this study incorporates elements of both AOAC 996.06 and AOCS Ce 1h-05[15]. The GC conditions, as well as the identification and quantification of trans fat in subsequent chromatography[15], are all subject to proposed amendments to AOAC 996.06.

chemicals

- Methanol- for methylation
- Toluene- as a catalyst
- Boron trifluoride – for esterification
- Hexane
- Distilled water

- **Procedure**
  1.<u>sample prepration</u>
  a) Collect the samples from different companies and location.
  weight the sample 2mg for fatty acid parameters.
  c) prepare the sample from FAME method for fatty acid profile.
  c.1) take 2mg (2,3 drops) sample in test tube.
  c.2) add **MTB** (1:1:1) in same test tube.
  c.3) take the sample at water bath for 1 hours at 60- 70^c, with proper shaking in every 15minute interval.
  c.4) after 1 hour take out the sample and cool down at room temperature.
  c.5) after cooling this, add 1ml distilled water and 1ml hexane.
  c.6) vortex this sample for 5 to 10 minutes.
  c.7) rest this for 2 to 3 minutes, then two layers are separated (upper layer of hexane and lower layer of water).
  c.8) pipette out the upper layer in vail.

- 2. <u>Instrumentation</u>
  d) then run these samples in column of gas chromatography.
  e) there is different detector for different parameters like FID for fatty acid profile and cholesterol, TCD for air purification (N_2, benzene), ECD for triglycerides.

f) different column for different parameters for fatty acid profile we use HP88 and supelco2560 and for cholesterol we use HP5.
g) detector detect and computer show the graph and peaks of different fatty acids.

Graphs

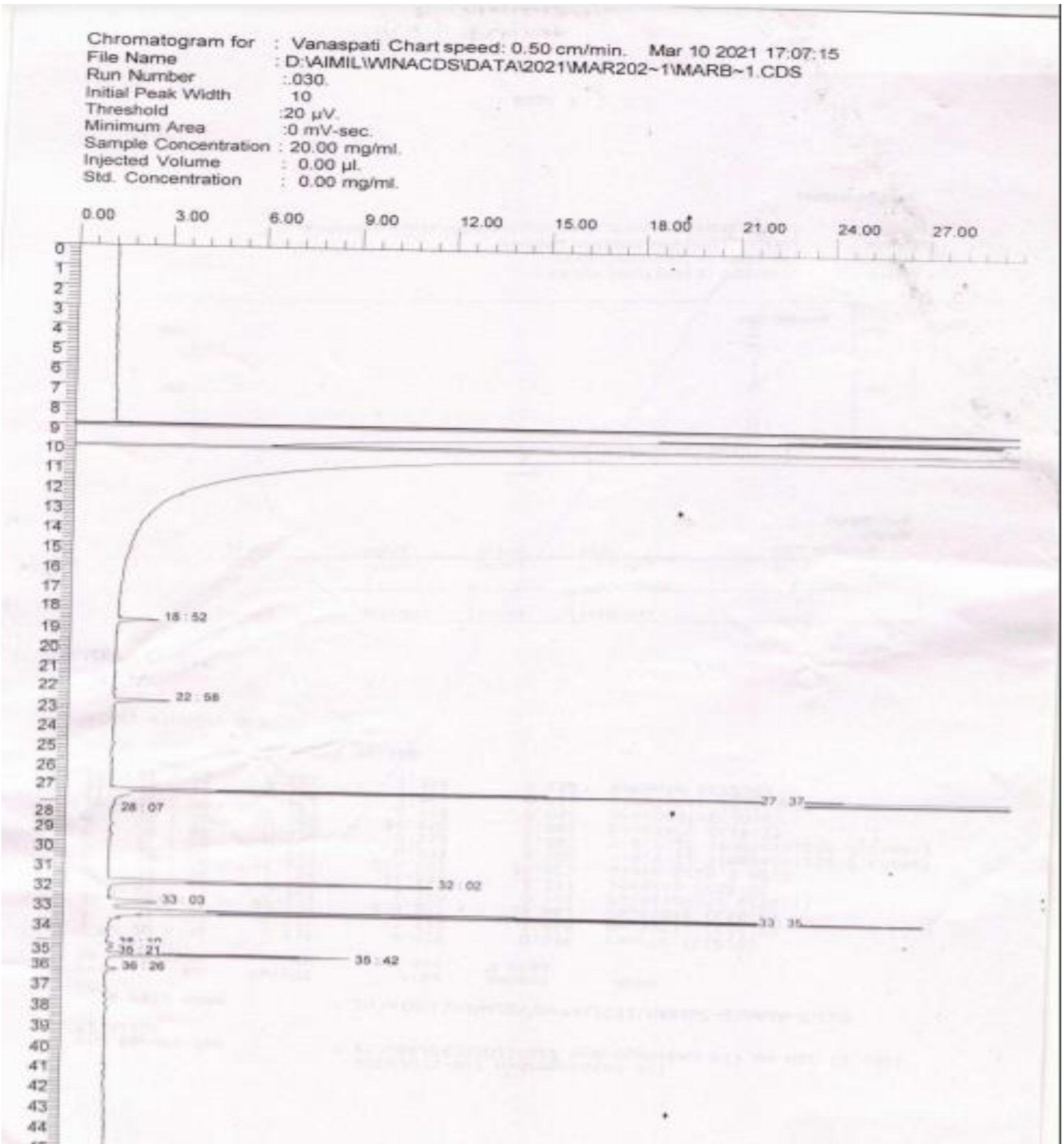
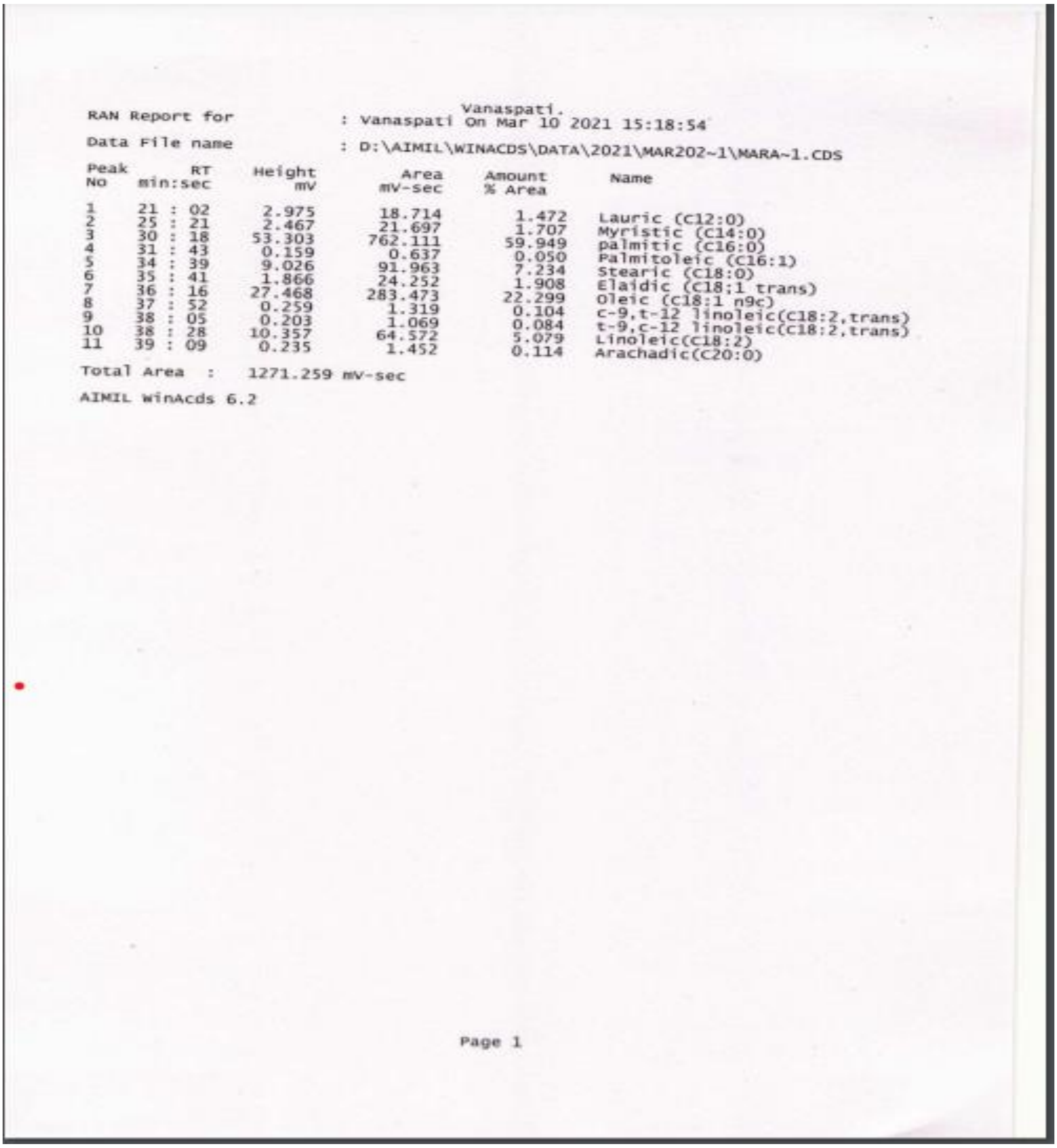


Figure – graph of vanaspati



RAN Report for : Vanaspati On Mar 10 2021 15:18:54 Vanaspati.

Data File name : D:\AIMIL\WINACDS\DATA\2021\MAR202~1\MARA~1.CDS

Peak No	RT min:sec	Height mV	Area mV-sec	Amount % Area	Name
1	21 : 02	2.975	18.714	1.472	Lauric (C12:0)
2	25 : 21	2.467	21.697	1.707	Myristic (C14:0)
3	30 : 18	53.303	762.111	59.949	palmitic (C16:0)
4	31 : 43	0.159	0.637	0.050	Palmitoleic (C16:1)
5	34 : 39	9.026	91.963	7.234	Stearic (C18:0)
6	35 : 41	1.866	24.252	1.908	Elaidic (C18;1 trans)
7	36 : 16	27.468	283.473	22.299	Oleic (C18:1 n9c)
8	37 : 52	0.259	1.319	0.104	c-9,t-12 linoleic(C18:2,trans)
9	38 : 05	0.203	1.069	0.084	t-9,c-12 linoleic(C18:2,trans)
10	38 : 28	10.357	64.572	5.079	Linoleic(C18:2)
11	39 : 09	0.235	1.452	0.114	Arachadic(C20:0)

Total Area : 1271.259 mV-sec

AIMIL WinAcds 6.2

Page 1

Figure – profile of vanaspati

Total fatty acid	SFA	MUFA	PUFA	TFAs
100.00	70.476	22.349	5.079	2.096

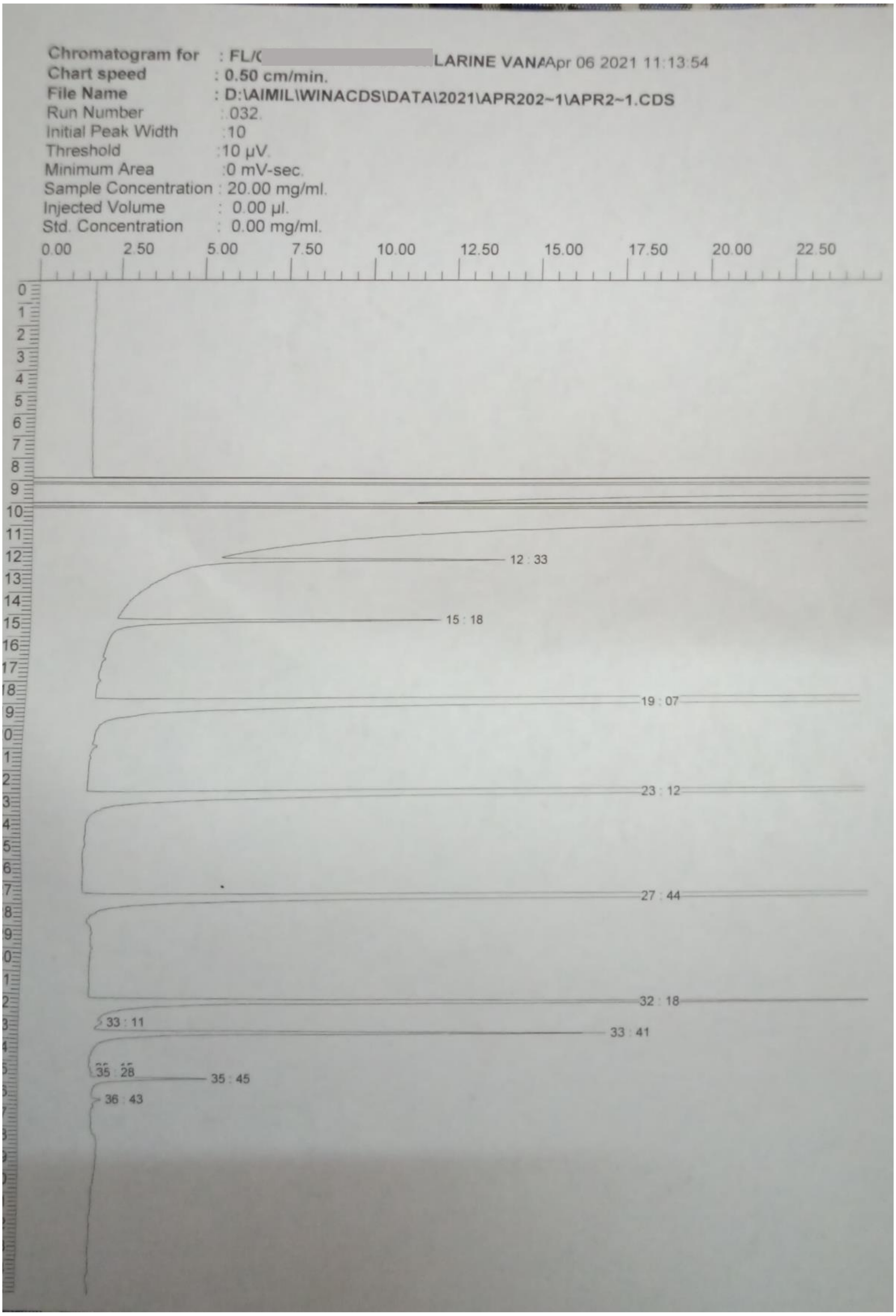
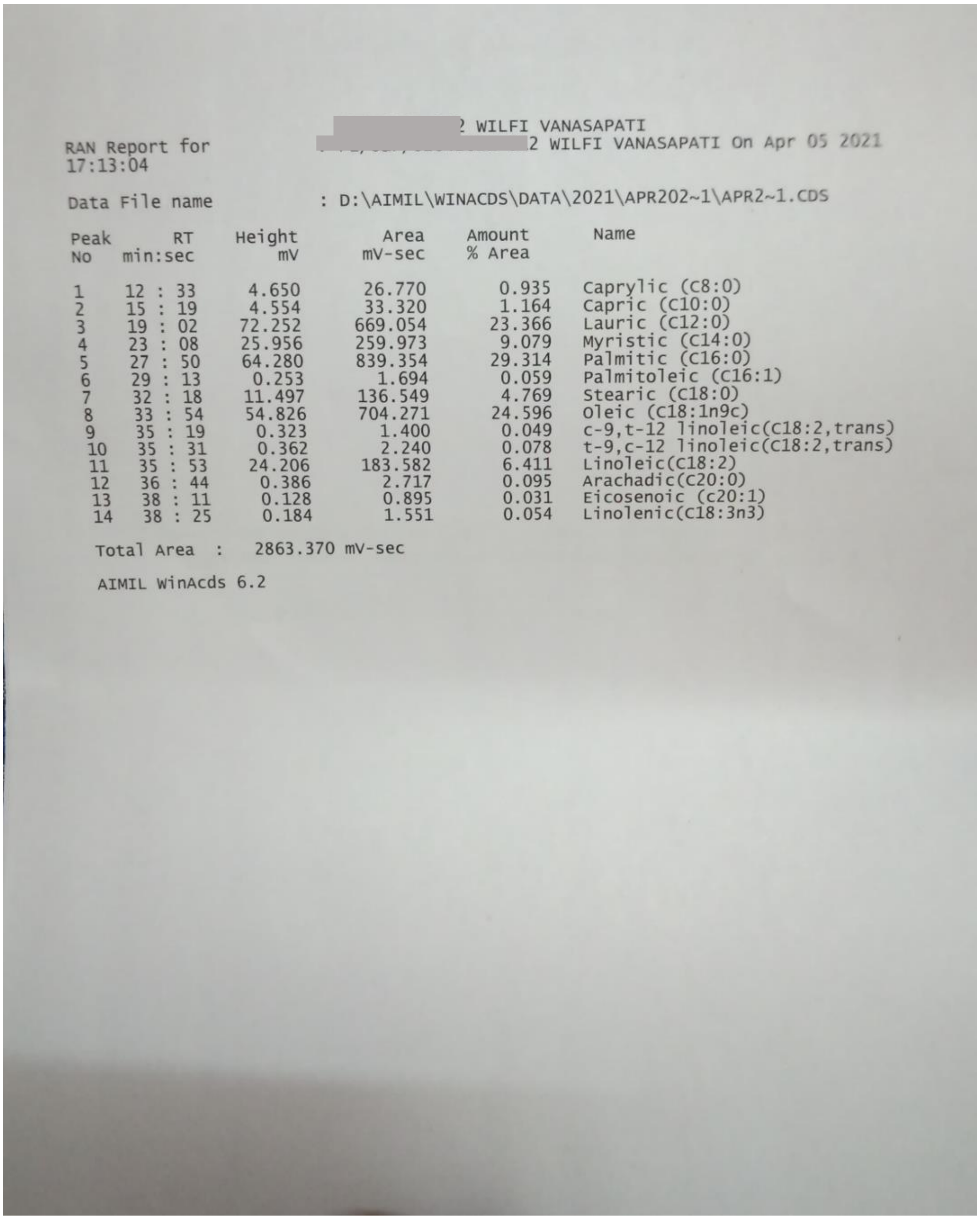


Figure – graph of wilarine vanaspati



[redacted] WILFI VANASAPATI
RAN Report for [redacted] 2 WILFI VANASAPATI On Apr 05 2021
17:13:04

Data File name : D:\AIMIL\WINACDS\DATA\2021\APR202~1\APR2~1.CDS

Peak No	RT min:sec	Height mV	Area mV-sec	Amount % Area	Name
1	12 : 33	4.650	26.770	0.935	Caprylic (C8:0)
2	15 : 19	4.554	33.320	1.164	Capric (C10:0)
3	19 : 02	72.252	669.054	23.366	Lauric (C12:0)
4	23 : 08	25.956	259.973	9.079	Myristic (C14:0)
5	27 : 50	64.280	839.354	29.314	Palmitic (C16:0)
6	29 : 13	0.253	1.694	0.059	Palmitoleic (C16:1)
7	32 : 18	11.497	136.549	4.769	Stearic (C18:0)
8	33 : 54	54.826	704.271	24.596	Oleic (C18:1n9c)
9	35 : 19	0.323	1.400	0.049	c-9,t-12 linoleic(C18:2,trans)
10	35 : 31	0.362	2.240	0.078	t-9,c-12 linoleic(C18:2,trans)
11	35 : 53	24.206	183.582	6.411	Linoleic(C18:2)
12	36 : 44	0.386	2.717	0.095	Arachadic(C20:0)
13	38 : 11	0.128	0.895	0.031	Eicosenoic (c20:1)
14	38 : 25	0.184	1.551	0.054	Linolenic(C18:3n3)

Total Area : 2863.370 mV-sec

AIMIL WinAcds 6.2

Figure – profile of wilarine vanaspati

Total fatty acid	SFA	MUFA	PUFA	TFAs
100.00	68.722	24.686	6.465	0.127

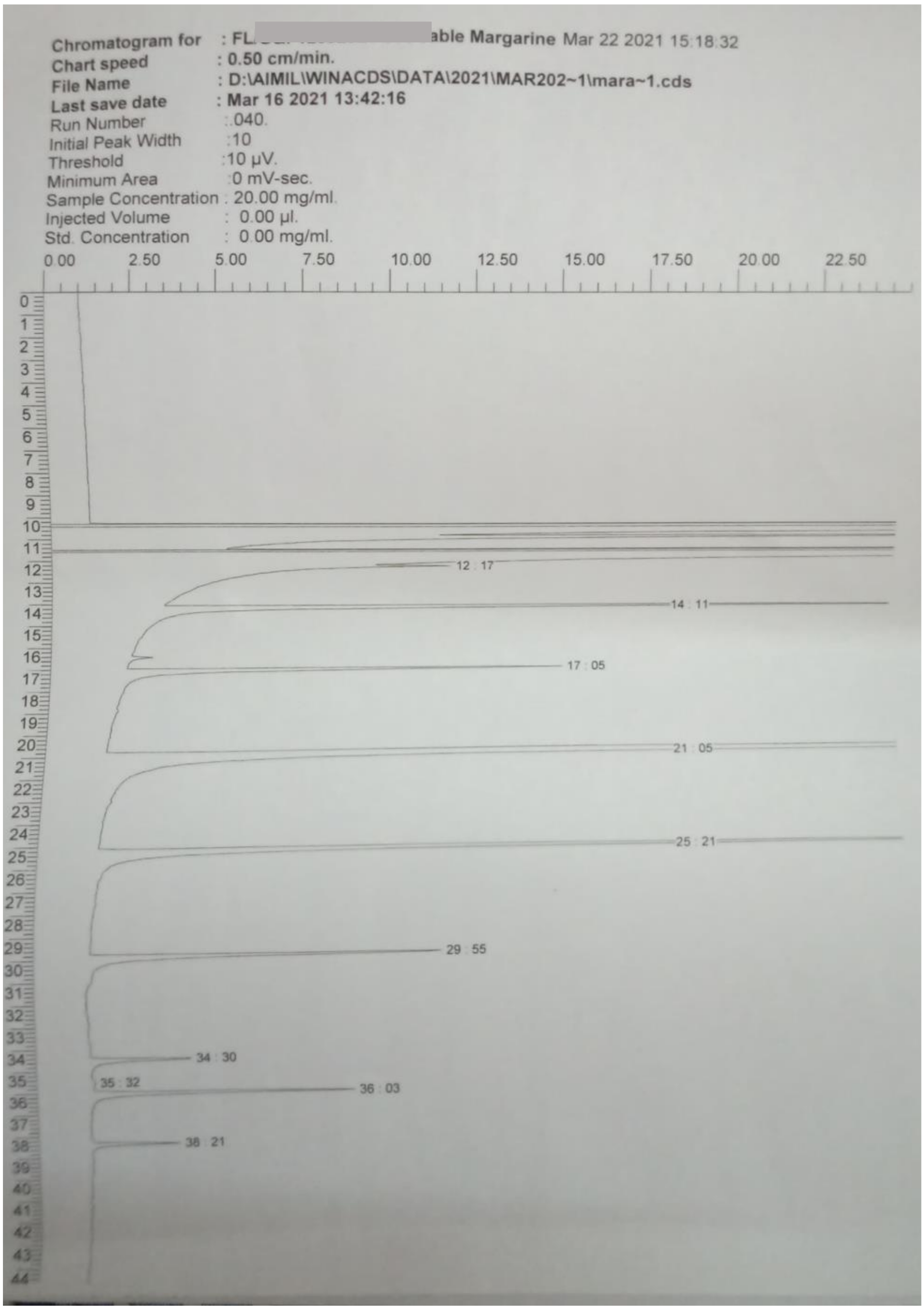
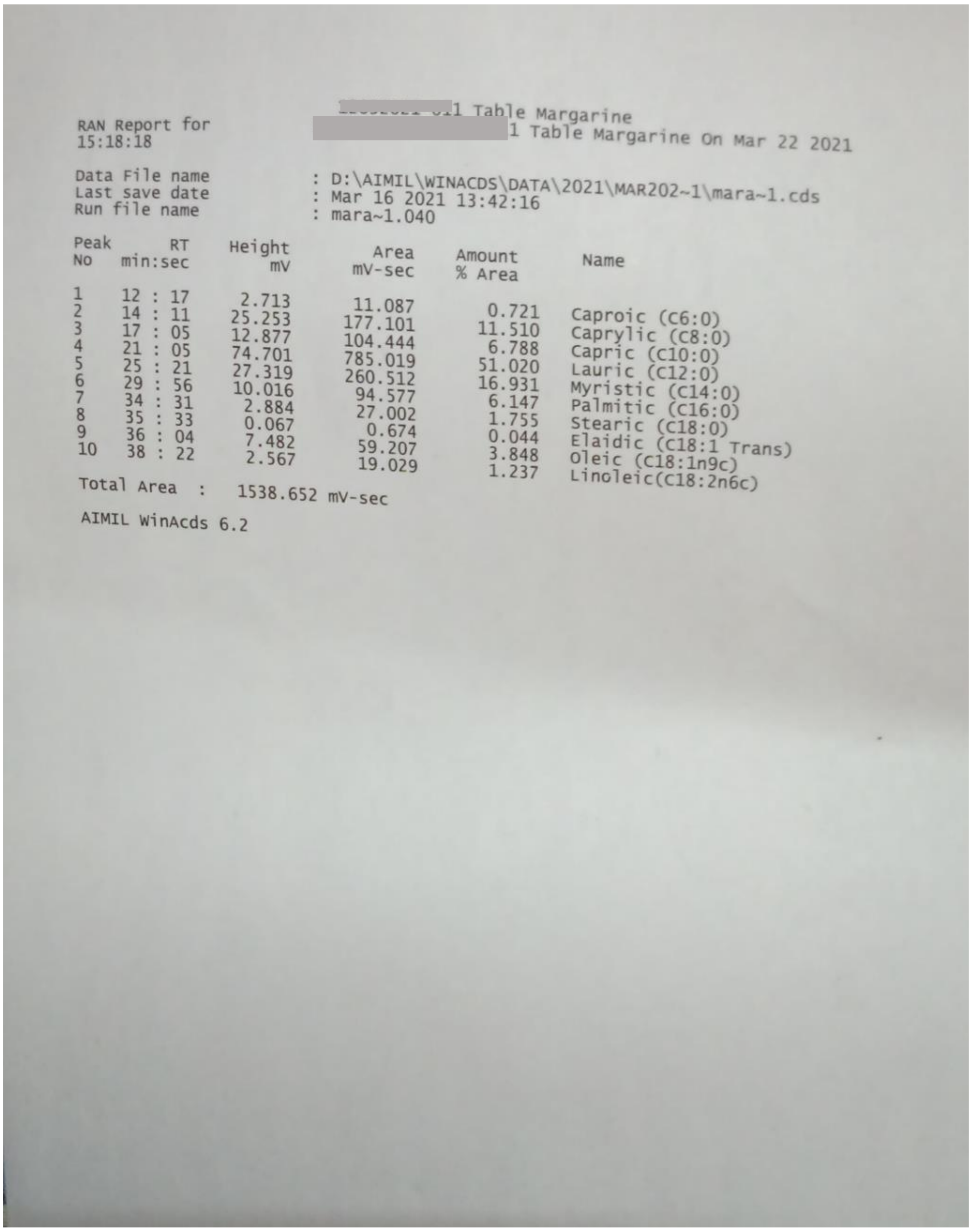


Figure – graph of table margarine



RAN Report for [redacted]1 Table Margarine
15:18:18 [redacted]1 Table Margarine On Mar 22 2021

Data File name : D:\AIMIL\WINACDS\DATA\2021\MAR202~1\mara~1.cds
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Peak No	RT min:sec	Height mV	Area mV-sec	Amount % Area	Name
1	12 : 17	2.713	11.087	0.721	Caproic (C6:0)
2	14 : 11	25.253	177.101	11.510	Caprylic (C8:0)
3	17 : 05	12.877	104.444	6.788	Capric (C10:0)
4	21 : 05	74.701	785.019	51.020	Lauric (C12:0)
5	25 : 21	27.319	260.512	16.931	Myristic (C14:0)
6	29 : 56	10.016	94.577	6.147	Palmitic (C16:0)
7	34 : 31	2.884	27.002	1.755	Stearic (C18:0)
8	35 : 33	0.067	0.674	0.044	Elaidic (C18:1 Trans)
9	36 : 04	7.482	59.207	3.848	Oleic (C18:1n9c)
10	38 : 22	2.567	19.029	1.237	Linoleic(C18:2n6c)

Total Area : 1538.652 mV-sec

AIMIL WinAcds 6.2

Figure – profile of table margarine

Total fatty acid	SFA	MUFA	PUFA	TFAs
100.00	94.872	3.848	1.237	0.044

Low fat and oil intake (less than 20% of daily calories)[22] raises the risk of vitamin E deficiency and essential fatty acid deficiency, which can lead to[17] unfavourable alterations in HDL and triglycerides. The following dangers have been linked to trans fatty acid consumption and human health[21].

Cardiovascular diseases

Breast cancer
Colon cancer
Diabetes
Obesity

Conclusion

Many baked items employ hydrogenated vegetable oils to improve taste and texture. Furthermore, these oils are more stable and resistant to oxidation, which occurs when fats are exposed to heat and causes them to break down.
Because of their unique properties, trans fatty acids provide various advantages for processed foods. These distinct structures have been linked to the potential that trans fatty acids[29] influence the development of a variety of health issues, including coronary heart disease, foetal and new born neurodevelopment and growth, childhood allergies, and so on[9]. Food makers are increasingly interested in zero- and low-trans fats, and the consumption of such products is growing. However, eliminating all TFA from the diet would be counterproductive because it would eliminate trans fats that are beneficial to health, such as vaccenic acid. Ruminant animal products, such as meat and dairy[2], are high in vital nutrients like protein, calcium, and iron, which are hard to come by in plants or other sources. The prohibition of these foods would be harmful to the general public, with the most catastrophic consequences for infants, who require a range of fatty acids for growth and development. To reduce transfat intake, four distinct measures are required[2]. For example, health care practitioners should educate their patients on how to reduce transfat intake. Trans fat-containing items should be identified and avoided by consumers[2]. Alternative fats should be used in food production and preparation by restaurants and food producers, and local, state, and national government agencies should support these efforts by implementing legislation that restricts transfat use. These actions should help minimise trans fatty acid consumption, resulting in significant health advantages[2]. Moreover, further research is needed to evaluate the health-related impacts of new TFA-free items, as it would be impossible to replace TFA with goods that are just as harmful, if not worse[9].

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