

# QUALITY ASSESSMENT OF FRYING OILS IN THE FORMAL AND INFORMAL FOOD PREPARATION SECTORS

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Dissertation submitted in compliance with the requirements for the  
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this 25 day of MAY 1998 at Technikon Natal.

## **DEDICATION**

**To my Family and Friends**

**An inspiration to lead a Healthy Life-style**

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## ABSTRACT

The demand for fried foods by the public and the number of people entering the fried food industry in the form of take-aways and fast food outlets both in the formal and informal sectors has increased tremendously.

Frying fats and oils are very expensive, used in large quantities and is the most important ingredient used in the preparation of fried foods. Due to the high cost of these frying fats and oils, majority of the formal and informal traders are using the frying fats and oils to its maximum in order to reduce the overall cost. This has resulted in the preparation of poor quality of fried foods.

Considering all of the above, the aim of the proposed research was :-

- (a) to determine the quality of the frying fats and oils used by both the formal and informal sectors by performing both physical and chemical analyses and compare these with similar analyses performed on the unused frying fats and oils in order to ascertain the degree of deterioration of the used frying fats and oils
- (b) to investigate the method of disposal of the used frying fats and oils.
- (c) to contribute in educating both the consumers and the suppliers of fried foods by bringing the findings of this research to the attention of the Durban Metro Health Department.

The used frying fats and oils were collected during the frying process by the environment health officer from the Durban Metro Health Department. These samples were placed in a refrigerator to prevent any further deterioration.

The used and unused frying fats and oils were analysed for, the Free Fatty Acid and Acid Value contents; the quantitative separation of Monoglycerides, Diglycerides and Triglycerides; the Refractive Index; the Peroxide Values; the concentrations of Polar and Non-polar Compounds; the Viscosity and the identification of the various fatty acid methyl esters present in the samples. The analytical methods used were followed from the American Oil Chemists Society (AOCS) Official Method Handbook.

The Free Fatty Acid and Acid Value results showed that twenty-five percent of the samples had a concentration of more than the maximum acceptable limit of 2.5%. It was evident that the types of food fried, the intermittent heating, frying



and cooling processes and the usage of the frying fats and oils over several days contributed to the high concentrations of free fatty acids and acid values.

The analysis of the glycerides showed a general trend where there was a gradual increase in the concentrations of Monoglycerides and Diglycerides and a decrease in the concentration of the natural Triglycerides as the usage of the frying oil increased. This was mainly due to the hydrolytic and oxidative reactions taking place in the frying medium during the frying process.

The Refractive Index values of most of the used frying fats and oils were close to the values of the unused frying fats and oils with an exception of a few samples which showed some differences.

The Peroxide Values indicated the degree of oxidation. Some of the peroxide values of the used frying fats and oils were very high in comparison with the peroxide values of the unused frying fats and oils. This showed that some of the frying processes were carried out under extremely unhygienic conditions.

The concentration of Polar Compounds is used to determine the abused state of the frying fat or oil samples and the acceptable maximum concentration, internationally, is 25%. The results showed that thirty percent of the used frying fat and oil samples had a Polar Compound concentration of more than 25% and these were mostly from the informal sector. Thirty percent of the samples had a concentration of between 20-25% of Polar Compounds and the remaining forty percent of the samples had less than 20% of Polar Compound contents. This showed that fifty-five percent of the samples had deteriorated, were unfit for further use and should have been discarded.

There was a significant difference in the viscosity values between the used and the unused frying oils. It was evident that the types of food fried and the duration of the frying process contributed to the increased viscosity readings.

The qualitative analysis of Fatty Acid Methyl Esters(FAME) was carried out to determine the presence of the different FAME in the frying fat and oil samples. The most common of the methyl esters present in abundance in all the samples were Palmitic, Stearic, Oleic and Linoleic Acid Methyl Esters. The samples that were extremely abused possessed large amounts of Myristic, Palmitoleic, Linolenic and Arachidic Acid Methyl Esters and these samples were mostly from the informal sector.

Responsible persons from both the formal and informal sectors were interviewed as to how they determined the life and the disposal method of the used frying fats and oils. Seventy percent from the formal sector depended on the colour, taste and appearance of the fried foods and the visual colour of the frying oil; thirty percent depended on the Standard Lovibond Colour Monitor.

With regards to the method of disposal, fifty-five percent of the formal traders sold the used frying fats and oils to their staff members or to the informal traders; fifteen percent filtered off the tiny food particles and added fresh oil whenever it was necessary; ten percent sold some of the used oil to their staff and used the remaining oil to prepare their curries and five percent dumped the used frying oils in their privately owned disposal site.

The response from the informal traders was very poor, disappointing and some of them even behaved aggressively. Fifty percent of those interviewed refused to divulge any information; thirty percent obtained the used frying oils from the formal sector and twenty percent did not discard the used frying oils.

The used frying oil samples were obtained without prior notification to the formal and informal food preparation establishments. The samples that were in a somewhat good condition, when collected, did not necessarily imply that the people responsible for these food frying outlets adhered to the strict control with regards to the replacement of the frying oils and to the monitoring of the frying process. The various analyses indicated that the general quality of the used frying fat and oil samples were extremely poor.

There is definitely an urgent need for the national and local health authorities to implement a strict control on the abuse and disposal of frying fats and oils and to educate both the suppliers and the consumers on the harmful effects on health caused by preparing foods in abused frying fats and oils and the subsequent consuming of poor quality fried foods.

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ALT	-	Alternate Method
AOAC	-	Association of Official Analytical Chemists
AOCS	-	American Oil Chemist Society
BF <sub>3</sub>	-	Boron Trifluoride
BHA	-	Butylated Hydroxyanisole
DNA	-	Deoxyribonucleic Acid
DPTG	-	Dimeric and Polymeric Triglyceride
EDTA	-	Ethylenediaminetetraacetic Acid ( Disodium Salt )
FAME	-	Fatty Acid Methyl Esters
FDA	-	The Food and Drug Association
✓ FFA	-	Free Fatty Acid ✓
GSFS	-	The German Society for Fat Science
GSH	-	Glutathione (reduced)
GSSG	-	Glutathione (oxidised)
HDL	-	High Density Lipoprotein
✓ INFORM	-	International News on Fats, Oils and Related Materials
JAOCs	-	Journal of the American Oil Chemists Society
KHP	-	Potassium Hydrogen Phthalate
KIO <sub>3</sub>	-	Potassium Iodate
LDL	-	Low Density Lipoprotein

$\text{Na}_2\text{S}_2\text{O}_3$	-	Sodium Thiosulphate
NADPH	-	Nicotinamide Adenine Dinucleotide Phosphate
✓ NaOH	-	Sodium Hydroxide
NFA	-	National Food Administration
PG	-	Propyl Galate
PUFA	-	Poly-unsaturated Fatty Acid
TBHQ	-	Tertiary butylated hydroquinine
TLC	-	Thin Layer Chromatography
USDA	-	The United States Department of Agriculture

## CHAPTER 1

### 1.0 GENERAL INTRODUCTION

#### 1.1 LOCAL FOOD PREPARATION OPERATION

Fried foods, such as potato chips, chicken, fish, meat and sausages form a major part of the diet of many people in South Africa. The quality and cleanliness of the frying oil or fat, the frying process and the type of friers used are very important factors in determining the quality of the fried foods produced. Many of the formal and informal food preparation outlets use inferior quality frying oils and in some cases these oils are unhealthy. During the process of frying and depending on the quality and temperature of the oil used a large amount of the frying oil is absorbed into the food with the result that this fried food together with the oil is eventually purchased by the public and eaten. Several factors that contribute to the "abuse" or deterioration of the frying oils or fats are;

- (a) The repeated and intermittent heating of the frying oil or fat.
- (b) Contamination of the frying oils by small food particles remaining in the frier.
- (c) The increase in the demand for fried foods.
- (d) The increase in the cost of fresh oil to replace the used oil.
- (e) The difficulty in disposing of the used oil.

Majority of the traders from the formal food outlets find that the most convenient method, and without incurring any additional cost, for the disposal of the used oil is to sell it to some of their lower paid staff-members or to the informal food preparation outlets.

The used oil from the formal sectors is abused even further by the informal traders because the oil is now subjected to very high uncontrolled temperatures and also exposed to the harsh atmospheric and unhygienic conditions.

On the other hand, some of the formal food frying outlets mix and collect the used oils, after frying the potato chips, fish, chicken, meat and sausages separately, into large twenty five litre plastic containers and sell them to certain "entrepreneurs" who then transfer the used mixed oil into smaller containers for re-sale to the informal outlets or to the poor domestic households in the townships and rural areas. These used frying oils are in great demand considering the high cost of the fresh unused oil sold in the supermarkets and in the local groceries stores.

Majority of the formal food preparation businesses use the large deep-frying type of electric friers which are also equipped with a thermostat control to regulate the temperature of the frying oil or fat and a suitable drainage system to drain the excess oil from the fried foods. This is extremely necessary as the formal food



preparation outlets are in operation for very long hours and produce fried foods on a very large scale due to the great demand for fried foods from the public.

The most common frying equipment used by the informal traders are either the round skottel or the rectangular solid plate type fuelled with a handy-gas cylinder. This type of heating equipment acts as a source of heat to fry the foods.

By using such type of friers and with no temperature control of the frying oil and the lack of drainage for the oil, most of the frying medium is absorbed into the fried foods and according to some of the consumers, such foods are tastier and pleasing in appearance. This is because the used oil obtained from the formal food frying sector also contains the food colourings and flavourings which were added to the foods prior to frying by the formal food preparation traders. This is also another factor that creates a greater demand for the used frying oils from the formal food preparation outlets, apart from the saving on the cost of purchasing fresh unused oil from the supermarkets or groceries stores.

Due to the high cost of fresh unused oil, most of the frying establishments have attempted to find a solution to bring about the savings on frying oil costs. This has unfortunately, resulted in the frying oils being heated repeatedly and used for several days thus causing the oil to be severely abused by thermal, hydrolytic

and oxidative degradation. The deterioration of the frying oil results in a substantial increase in the concentration of total polar compounds and other toxic products which are detrimental to human health.

Several chemical reactions take place during the frying process forming volatile compounds which are lost from the hot frying oil and non-volatile compounds which steadily increase in concentration. The non-volatile compounds are often of high molecular weight and polar and their presence has been used by several researchers to define the quality of used or abused oils.

## 1.2 NATIONAL AND INTERNATIONAL SURVEYS

The Laboratory of the Government Chemist, in collaboration with the UK Ministry of Agriculture, Fisheries and Food, conducted a survey in the London area and analysed 50 used and 50 unused frying oil and fat samples from almost 100 cafes, restaurants, hospitals and school kitchens. The average polar compound concentration determined in the unused frying oil samples ranged from 0,4% to 6,4%, whereas, the used frying oil samples had a polar compound content in the range from 4% to 46% (Lumley, 1988).

The harmful effects of polar compounds from the abused frying oils has been studied for more than 40 years. Researchers have found that the intake of abused frying oils with a concentration of more than 50% total polar compounds

has been responsible for many diseases and sickness. These overheated abused frying oils caused severe irritation of the gastro-intestinal tract, diarrhoea, growth retardation and in some cases even death when they were fed to animals. On the other hand, the Unilever Laboratory in Germany performed experiments over a period of 10 years by feeding animals with frying oils which were heated under controlled temperatures and hygienic conditions and containing between 10 and 20 percent polar compounds showed no adverse effects. Results from these experiments had shown that the animals did not experience any ill-effects even with the addition of large amounts of the frying oils in the diet (Billek, 1985).

The German Society for Fat Research and the Unilever Laboratory in Germany, having performed research on over 400 used frying oil samples, recommended that frying oils and fats containing more than 30% total polar compounds should be regarded as being deteriorated and therefore unfit for human consumption. This limit of 30% polar compounds in frying oils has been generally accepted as the point at which the frying oil is definitely unfit for further use, but rather, to be discarded (Billek, 1985).

The Lipid Biotechnology Laboratory of the Department of Microbiology and Biochemistry at the University of the Orange Free State and the Environmental Health Division of the Municipality of Bloemfontein conducted a survey, similar to

that conducted by the Laboratory of the Government Chemist and the UK Ministry of Agriculture, Fisheries and Food in the London area, on the quality of used frying oil from 54 cafes, restaurants and similar establishments.

The total polar compound concentration determined in the 54 used frying oil samples ranged from 1% to 57%. 37 samples had a concentration of less than 30% total polar compound which, according to the Unilever Laboratory in Germany, was the acceptable limit and 17 of the samples had a concentration of more than 30% total polar compound which indicated that these frying oils had deteriorated, and therefore, according to the Unilever Laboratory in Germany, were unacceptable for human consumption. A matter of great concern was that 6 samples had a concentration of more than 50% total polar compound indicating that these frying oils were extremely abused (Kock, 1994).

According to the same survey conducted by the University of the Orange Free State, 15 of the 17 used frying oils containing more than 30% total polar compound were either sold or given to employees or people from the underprivileged communities in the Bloemfontein area for further use in the frying of foods. The survey also indicated that about 250 tons of frying oil are used annually in the Bloemfontein area (Kock, 1994).

Studies were conducted on the quality of frying oil samples from 52 catering organizations of the French Military Force based in Germany. For each oil, the colour, acidity, extinction value at 230nm and 270nm, percent polar compounds and overall quality were assessed. Results indicated that sixty five percent were satisfactory, seventeen percent required changing and eighteen percent were unfit for human consumption (Denry, 1993).

The quality attributes of commercially used frying oils collected from street vendors in Taipei was determined. The oil samples were analysed for acid value, viscosity, dielectric constant changes, alkali colour test, total polar content and polymer content. Since it was generally accepted that oil is temperature abused when the total polar content reaches 25%, the cut-off value corresponding to 25% total polar content was also determined. The results indicated that more than fifty percent of the oil samples collected from the street vendors were temperature abused (Hau, 1987).

### **1.3 MAJOR DISASTERS CAUSED BY ABUSED FRYING OILS**

The National Department of Health and the Provincial and Local Authorities in South Africa have only recently as 1994 regulated the monitoring of abused frying oils and become aware of the health hazards caused by the use of deteriorated frying fats and oils for the preparation of fried foods (Kock, 1994).

Many other countries have experienced major food poisoning disasters caused by chemical compounds produced from extremely abused frying fats and oils.

A major crisis occurred in Madrid, Spain in May 1981 over a period of three months where contaminated cooking oil used in the preparation of foods resulted in the hospitalisation of about 20 000 people and the death of about 340 people. The most common symptoms were fever, respiratory problems, coughing, skinrash, nausea and vomiting, headache, muscle pain and diarrhoea.

The Directorate General of Public Health in Madrid set up working groups to investigate the cause of the epidemic. Tests were, at first, conducted on the cooked foods for microbiological contamination. However, after carrying out an extensive investigation which also included the results of questionnaire studies, it emerged that the contamination was due to the use of cheap unlabelled and used cooking oil which was sold to the local inhabitants by vendors as olive oil in five litre plastic containers, the possible contaminant being aniline.

One thousand and five hundred people were affected and 200 people died in Bombay in 1971 when rape-seed oil used for cooking was contaminated with industrial machine oil. More than 800 people died in Chile in 1958 due to the use of toxic frying oils.

Cooking oil contaminated with tryptophan metabolites, which are amino acids that become toxic as the concentration increases affected 2800 people and caused the death of 712 in the United States of America in 1989 (WHO, 1994).

Since contaminated or deteriorated cooking fats and oils were the primary cause for all the major disasters, the effects of contaminated and abused frying oils used in the manufacture of fried foods is only now being investigated in South Africa.

Considering the investigation conducted by the University of the Orange Free State in the Bloemfontein area and the research which I am involved in at the present moment in the Durban and surrounding areas, it can be concluded that majority of the owners and employees in the food frying industry have a don't care attitude towards adhering to the regulations regarding the use and sale of frying oils and fats and that South Africa is sitting on a potential time bomb unless drastic action is implemented by the National and Provincial Health Authorities.



## 1.4 LEGISLATION

The Minister of Health published a draft regulation which referred to the detailed definitions of edible fats and oils, fatty acids, food additives, glycerides, lipids, mineral oils, phosphotides, polar components, polymerised triglycerides and triglycerides.

Special provisions were made in the regulation which applied to edible fats and oils and mixtures thereof which were intended for final consumption and catering purposes or which were used as ingredients in the manufacture of foodstuffs. These provisions were :

1. There is to be no mineral oils present in edible fats and oils. The edible fats and oils may contain antioxidants as permitted by Government notice dated 3 June 1977 and colourants as permitted by Government notice dated 6 May 1977 and amended on 9 September 1983. The standards for the purity and composition of fats and oils are those laid down in the latest edition of Codex Alimentarius Standards for Fats and Oils for the British Pharmacopoeia.

2. The edible fats and oils which were used for the frying of foods were deemed to be harmful or injurious to human health unless they contained less than 16% polymerised triglycerides and/or 25% polar components. The Director-General of Health invited interested persons to submit any substantiated comments or

representations on the proposed regulations as mentioned above. These regulations have now been in operation as from 1 April 1996 (Government Gazette, 27 October 1995).

## 1.5 AIM AND OBJECTIVES

The aim of the proposed research was to contribute, in collaboration with the health workers in the Durban Metro Health Department, to the education of the consumers and the suppliers of fried foods on the possible harmful effects on the consumption of foods prepared in poor quality frying oils and fats.

The objectives of the proposed research were to:

- (A) To determine the quality and constituents of the used frying oils from both the formal and informal food preparation sectors and to compare them with that of the fresh unused frying oil.
- (B) To investigate the method of disposal of the used frying oils from the formal and the informal sectors.
- (C) To, indirectly, gain knowledge of the quality of the fried foods prepared and sold by the formal and informal sectors to the public from the analytical results obtained on the frying oil samples.

- (D) To determine what method or methods which have been established or new can be used to measure frying oil quality, with assessment of the feasibility of using such methods on the spot.

## CHAPTER 2

### 2.0 LITERATURE REVIEW

### 2.1 PHYSICAL AND CHEMICAL CHANGES IN FATS AND OILS DURING THE FRYING PROCESS

Deep-fat frying is a complex method of food preparation during which a variety of chemical reactions take place in the frying oil. In frying, the food is submerged in fat or oil heated in the presence of air, and as such, is exposed to the action of the three primary agents which cause the most drastic changes in the structure of the frying fat or oil, namely:

- (a) Moisture from the food, giving rise to hydrolytic degradation.
- (b) Atmospheric oxygen entering the oil, giving rise to oxidative degradation.
- (c) The high temperature at which the frying operation takes place, giving rise to thermal degradation.

The existence of the degradation compounds in the frying medium results in a series of physical and chemical changes, some of which are easily observed and are as follows (Gutierrez et al).

- (a) Variation in organoleptic characteristics, caused by the development of aromas and tastes typical of fats and oils heated to high temperatures when foods are fried in them.

*Chemistry*

- (b) An increase in the viscosity and density of the oil as a result of polymerisation reactions. *physical*
- (c) The *physical* darkening of the frying medium due to the *chemical* presence of unsaturated carbonyl compounds or to non-polar compounds of food soluble in the fat.
- (d) The tendency of *chemical* foam formation also related with polymerisation products and amphophilic substances from the foods.
- (e) The *chemical* increase in acid value due mainly to hydrolytic reactions.
- (f) The decrease in iodine value due to the breakdown of the double bonds caused by polymerisation and cyclization reactions (Gutierrez et al).

When a moist food is placed in oil at high frying temperatures, air and steam are evolved initiating a chain of interrelated reactions. The natural triglycerides comprising an oil or fat and considered to be non-polar material are hydrolysed by the steam, resulting in the formation of free fatty acids, monoglycerides, <sup>ch</sup> diglycerides, glycerols and oxidised triglycerides, while the air released in the frying system initiates a cycle of oxidation reactions resulting in the formation of free radicals, oxidised monomers, oxidative dimers and polymers, non-polar dimers and polymers; volatile compounds such as hydrocarbons, aldehydes, ketones, alcohols and acids and finally the high frying temperatures applied on the oil results in the formation of cyclic monomers, dimers and polymers.

Some of these volatile or non-volatile compounds which are soluble in the oil are defined as polar compounds. The repeated and intermittent heating and cooling process of the frying oil also increases the degradation of the oil, probably owing to peroxide formation and decomposition during the heating, frying and cooling cycles. It has been claimed that a frying fat or oil which has a polar content of over 25% is unfit for further use and must be discarded (Cuesta, 1993).

During the frying process the concentration of the degraded products gradually increases and the quality of the oil deteriorates until it is unfit for further use. The quality of the food fried in the oil correspondingly decreases until it is unacceptable. Several countries have placed legal limits on the amount of total polar material that may be present in an oil used for deep-fat frying.

It is common practice for restaurant owners and managers to filter the oil used for deep-fat frying to remove food debris, which may accelerate the decomposition of the oil. The removal of food debris alone is known as passive filtration and the removal of soluble impurities by adsorption is known as active filtration. A much better quality of fried food is obtained and the life of the frying oil is even extended further after the frying oil undergoes both active and passive filtration (Yates, 1993).

Lipid oxidation is a normal biological process during which energy is obtained from the fat. Oxidation reactions that occur in foods are referred to as autooxidation and similar reactions that take place in the body are referred to as peroxidation. Both of these oxidation reactions are harmful to health.

Highly oxidised foods possess a rancid smell or taste and, therefore, people will avoid consuming such foods. On the other hand, foods that are slightly or moderately oxidised are not discarded but consumed. The question is how much of this slightly oxidised food can be consumed before being concerned of its harmful effects to health. There have been no reports published or any research carried out to determine as to what amount of the oxidation products, after having been consumed, will cause ill-health (Haumann, 1993).

Lipid oxidation causes a loss of the essential and natural fatty acids found in foods, nutritional value of foods as well as flavour deterioration, impaired colour and texture and highly oxidised foods have a negative effect on health.

Unsaturated fatty acids are the main targets of oxygen attack in addition to other compounds such as sterols, carotenoids and aromatic compounds. The reaction between oxygen and lipids does not take place spontaneously, but instead, it is initiated either by the formation of free radicals from the lipids or by the formation of active oxygen species that are able to react directly with the lipid molecule.

Some of the factors that contribute to the oxidation of the foods are enzymes, metal and metal compounds, light and heat. Oxidation can also occur in raw materials and during the processing of foods. In order to control the rate of oxidation, it is essential to limit the amount of oxygen and light during the processing and packaging of foods. Other methods to limit the rate of oxidation is to render the enzymes inactive, store the foods at low temperatures or to add an antioxidant in the frying oil or fat during the frying process (Haumann, 1993).

\* Lipid oxidation occurs very rapidly in deep-fat frying because of the high temperatures which these oils and fats are subjected to. Lipid oxidation remains a major problem in the food industry and an important cause of food quality deterioration.

It has been shown that thirty percent of the frying medium is oxidised after only 72 hours of frying and that rats, having been fed with highly oxidised frying fat showed a decrease in growth, an increase in liver weight and deposits of fatty tissues.

During the frying process some of the fat is absorbed into the fried food, thus, studies have shown that the concentration of oxidation products determined in the absorbed fat in the fried food was the same as that determined in the bulk of the frying medium (Haumann, 1993).



Free radicals are highly energized molecules that contain an unpaired electron. Many, although not all, radicals are unstable. They are produced through normal biological and environmental processes, involving oxygen and can trigger chain reactions that produce more free radicals. Under a healthy state there is normally a balance between the amount of free radicals produced in the body and sufficient antioxidants to protect against them. Free radicals are formed constantly by the body's normal use of oxygen such as in respiration and cell mediated immune functions. They are also found in frying oils and fats, environment pollutants, cigarette smoke, vehicle exhaust fumes, radiation or ultraviolet light, air pollutants, pesticides and certain industrial solvents. Common oxygenated free radicals are listed in Table 2.1.

Free radicals can damage cell membranes and other vital cell components, such as genetic material in the cell nucleus, and can inactivate enzymes. Damage to body cells and molecules by oxygen containing free radicals has been implicated in a wide variety of diseases. Highly unsaturated fatty acids are more susceptible to peroxidation than saturated fatty acids.

A free radical which attacks an unsaturated fatty acid creates a lipid radical which then reacts with another unsaturated fatty acid creating a radical-mediated chain reaction that can result in damage to a lipoprotein or cell membrane.

Vitamin E is often called a chain-breaking antioxidant because it neutralizes the free radicals that could initiate or propagate an oxidative-chain reaction. Highly unsaturated fatty acids, such as those found in fish oils, are most susceptible to peroxidation followed by the unsaturated fatty acids, primarily linoleic or linolenic acid, found in many vegetable seed oils (Jacob, 1994).

**Table 2.1 Common Oxygenated Free Radicals**

<u>Species</u>	<u>Common name</u>	<u>Half-life ( 37° C)</u>
$\text{HO}^\bullet$	Hydroxyl radical	1 nanosecond
$\text{HO}_2^\bullet$	Hydroperoxyl radical	Unstable
$\text{O}_2^\bullet$	Superoxide anion radical	Enzymatic
$\text{RO}^\bullet$	Alkoxyl radical	1 microsecond
$\text{ROO}^\bullet$	Peroxyl radical	7 seconds
$\text{NO}^\bullet$	Nitric oxide	5 seconds
$^1\text{O}_2$	Singlet oxygen	1 microsecond

## 2.2 INTERNATIONAL REGULATIONS OF FRYING

### FATS AND OILS

A survey was carried out during the period 1990 to 1992 with regards to regulations and standards pertaining to frying fats and oils and fried foods in other countries. Fifty-two countries were contacted but responses were received from thirty-one countries. Although several countries responded by stating that they have no specific laws or regulations for frying fats and oils, there were some countries that have specific laws, regulations or standards, whilst other countries enforce measures for practical control of frying fats and oils in restaurants and fast-food establishments. The information received from some of the countries are outlined below.

#### 2.2.1 Regulation on Frying Fats and Oils in Austria

The regulations mentioned in the Austrian Codex Alimentarius (Austrian Foodstuffs Book) states that frying fats and oils should not exhibit an unpleasant odour and taste, have an unacceptable appearance (dark colour and foaming) or have high level of carbonaceous residue and also includes the following specific standards :-

- (a) The acid value should not be more than 2,5%.
- (b) The smoke point should not be below 170° C.

- (c) The total polar compound concentration must not be more than 27% or the oxidised fatty acids insoluble in petroleum ether must not be more than 1%.
- (d) The frying fats or oils should not be heated above 180° C.

### **2.2.2 Regulation on Frying Fats and Oils in Australia**

The National Food Authority established in August 1992 is responsible for setting food standards that are enforced by the states and territories under their own food laws. The Australian Defence Force Specification 5-5-2 (Nov. 1984) requires that deep-fat frying be carried out in accordance with good manufacturing practice and comply with state and territory food regulations and that solid fats used for deep-fat frying should comply with the following regulations :-

- (a) The moisture content must not be more than 3g per kilogram (0,3%).
- (b) The free fatty acid content must not be more than 1g per kilogram (0,1%).
- (c) The slip-melting point must be between 38° C and 49° C.
- (d) The peroxide value must not be more than 2 meq per kilogram (2 mmol per kg).
- (e) The gallate content must not be more than 0,1g per kilogram (0,01%).
- (f) Clean flavour and absence of objectionable odour.

The liquid fats and oils for deep-fat frying should comply with similar requirements for moisture, free fatty acids, peroxide value and gallate content. Saturated fatty acid content should not exceed 500g per kilogram (50%) of total fatty acids. Fats and oils for deep frying should not contain mineral oil or more than 50g per kilogram (5%) of erucic acid.

The Victoria Health Department points out that municipal councils are responsible for the surveillance of food premises. Frying oils are subjected to collection and analysis for iodine value, saponification value, unsaponifiable matter, acid value and peroxide value as well as qualitative tests for adulterants.

Some local councils are using Oxifrit Test Kits to determine the degree of deterioration of frying fats and oils in kitchens and bakeries.

### **2.2.3 Regulation on Frying Fats and Oils in Belgium**

Quality standards for edible fats and oils was established by a royal decree in 1974. In 1978 the addition of additives such as antioxidants, including up to 3 mg per kilogram of dimethylpolysiloxane was permitted in frying oils and fats. A law issued in 1988 forbids the preparation of fried foods in frying fats heated above 180° C. Fats and oils intended for frying are required to be labelled "Oils for Frying" and if dimethylpolysiloxane is added, it must be mentioned on the label.

The Authorities have stated that the frying establishments must comply with the following regulations :-

- (a) The Acid Value concentration to be not more than 2,5%.
- (b) The dimeric and polymeric triglycerides content to be not more than 10%.
- (c) The total polar compound content to be not more than 25%.
- (d) The viscosity must not be greater than 37mPa-sec for food fats and not greater than 27mPa-sec for food oils, both determined at 50° C.
- (e) The smoke point must not be below 170° C.
- (f) Frying oils and fats may not contain more than 2% linolenic acid.
- (g) All frying equipments and friers must be thermostatically controlled.

#### **2.2.4 Regulation on Frying Fats and Oils in Finland**

The National Food Administration of Finland issued a circular letter in 1991 to all public health boards in the country outlining procedures for the sampling, analysis and the regulations applicable to frying fats and oils.

- (a) The colour, odour, and taste must not be less than 1, on a scale of 1 to 5.
- (b) The total polar compound content must not be greater than 25%.
- (c) The acid value must not be more than 2,0% for oils and 2,5% for fats.
- (d) The smoke point must not be below 180° C for oils and 170° C for fats.
- (e) The Fritest must not be more than 2, on a scale of 1 to 4.
- (f) The frying equipment to be cleaned regularly and made of stainless steel.

### **2.2.5 Regulation on Frying Fats and Oils in France**

A constitutional law passed in 1905 empowered the French Authorities to regulate the preparation of fried foods and to specify conditions for analysis. A 1973 regulation specified that deep-frying fats should not contain more than 2% linolenic acid.

Synthetic antioxidants such as butylated hydroxyanisole, butylated hydroxytoluene and gallates and the natural tocopherol concentrates are permitted in fats and oils intended for industrial use whereas silicone additives are prohibited. A Decree No. 86-857 of 18 July 1986 specifies that frying fats and oils containing more than 25% total polar compounds are unfit for human consumption.

### **2.2.6 Regulation on Frying Fats and Oils in Germany**

There are no specific laws or regulations in Germany for control of frying fats and oils. However, the recommendations resulting from the two symposia held in 1973 on frying fats are used to control the quality of frying oils. The Federal Institute for Fat Research in Munster revealed that many restaurants were abusing fats, particularly those frying meaty foods. According to the recommendations, used frying fats and oils are considered to be deteriorated if :-

- (a) The taste and flavour is unacceptable.
- (b) The smoke point is below 170° C.

- (c) The content of oxidised fatty acids insoluble in petroleum ether is over 0,75%.
- (d) The total polar compound concentration is more than 27%.

### **2.2.7 Regulation on Frying Fats and Oils in Hungary**

There are no mandatory regulations for the control of frying fat quality. Standard No. Msz-08-1907-87 established on 6 January 1988 and recommended by The National Institute of Food Hygiene and Nutrition have suggested the following conditions :-

- (a) The frying fat is unusable if the total polar content is more than 30%.
- (b) Iron and copper based friers should not be used.
- (c) The frying temperature should be kept between 160° C and 180° C.
- (d) Frying fats having a smoke point below 180° C should be discarded.
- (e) Sunflower oil may be used for 8 to 10 hours, corn oil may be used for 10 to 13 hours and lard may be used for 18 to 20 hours if treated carefully.
- (f) After frying, the oil should be filtered and stored at low temperature.

### **2.2.8 Regulation on Frying Fats and Oils in Israel**

Although Israel has no specific regulations for cooking and frying oils, guidelines published by the Swedish National Food Administration are recommended for application by Food Control Administration inspectors. Israel's Food Control



Administration submitted a request to the Standards Institution of Israel in 1992 that a requirement for total polar compounds be added to the vegetable oil standard, but the request was rejected.

### **2.2.9 Regulation on Frying Fats and Oils in Italy**

The Ministry of Health issued a regulation on 01 January 1991 to prevent possible health risks to consumers from improper or excessive use of fats and oils for frying. The regulation specifies the following :-

- (a) Use only those fats and oils for frying that are resistant to heat.
- (b) Avoid frying temperature above 180° C.
- (c) The total polar compounds content should not be more than 25%.
- (d) Prepare the food to be fried properly, avoiding as much as possible the presence of water and the addition of salt and spices, which accelerates changes in the frying fats or oils.
- (e) Allow the excess oil to drain from the food after frying to avoid absorption of excessive oil by the food.
- (f) Change the oil frequently, check the quality of the fat or oil during frying, do not use the oil too long as indicated by the darkened colour, viscosity and the tendency to smoke.
- (g) Filter the oil if it will be reused and clean the filter and frier, charred crust, viscous oily residue or old oil will accelerate alteration of the oil.

- (h) Avoid the addition of fresh oil to the used oil as the fresh oil is altered rapidly when in contact with the used oil.
- (I) Protect the frying fats and oils from light.

#### **2.2.10 Regulation on Frying Fats and Oils in Japan**

There are no formal regulations controlling the quality of frying oils and fats. However, with regard to food frying establishments, the following guidelines are available for determining when to discard the frying fats and oils.

- (a) If the smoke point of the frying fat or oil is less than 170° C.
- (b) If the acid value of the frying medium is more than 2,5%.
- (c) If the carbonyl value of the frying oil or fat is more than 50%.

#### **2.2.11 Regulation on Frying Fats and Oils in Luxembourg**

There are no specific regulations for frying fats. However, the general regulations for all foods also apply to frying fats. For practical control in food establishments that prepare and sell fried foods, the food inspectors use E. Merck's Fritest and if this test result indicates the frying fat is deteriorated, then the frying fat is further tested for free fatty acids, total polar compounds, taste, colour, odour and appearance.

### **2.2.12 Regulation on Frying Fats and Oils in The Netherlands**

The food regulations are enforced by 16 food inspection services, each covering an inspection area of about one million inhabitants. The inspectors sample the frying fats or oils in restaurants, snack bars, fish shops, hotels and any other food establishments that prepare and sell fried foods to the public. The frying oil samples are brought to the laboratory where they are checked for odour, taste, acid value and the concentration of dimeric and polymeric triglycerides (DPTG). The frying fat or oil is unfit for human consumption if the acid value is greater than 4,5 and / or the DPTG concentration is higher than 16%.

### **2.2.13 Regulation on Frying Fats and Oils in Norway**

The regulations in Norway require that foods to be free of pollutants and toxic substances and specify that only tocopherol and citric acid may be added as antioxidants to the frying fats and oils. For practical control in restaurants and fast-food establishments, the Norwegian inspectors use organoleptic evaluations or the Fritest.

### **2.2.14 Regulation on Frying Fats and Oils in Portugal**

There are no specific regulations for frying fats and oils. However, the Ministry of Agriculture's Food Quality Institute examines frying and cooking fats and oils for colour and odour and by the Fritest, Oxifrit Test and the Veri-Fry Colorimeter

Test. If the results from these tests show that the frying medium is deteriorated, the frying oil or fat is then analyzed for content of total polar compounds.

### **2.2.15 Regulation on Frying Fats and Oils in Spain**

The Royal decrees of 1981 and 1983 regulate the transportation, processing and commerce of edible fats and oils but are not applicable to frying. However, a decree in 1988 to protect consumers specifies that frying fats and oils :-

- (a) Must not contain foreign compounds.
- (b) Must contain less than 25% total polar compounds.
- (c) Should satisfy sensory evaluations.
- (d) Must not alter the quality of the fried food.
- (e) The used frying fat or oil must not be sold to prepare food products.

### **2.2.16 Regulation on Frying Fats and Oils in Sweden**

The National Food Administration (NFA) issued a document in 1989 outlining the following guidelines on the handling of frying fats.

- (a) The fats and oils must be discarded once they start to smoke or foam. Use the Food Oil Sensor or the Oxifrit Test as an indicator.
- (b) The frying fat must be filtered and stored at a lower temperature in a covered stainless-steel vessel and the frying equipment cleaned once a day.

- (c) The frying temperature should be between 160 - 180° C. The product absorbs more fat at lower frying temperatures and the fat deteriorates rapidly at higher frying temperatures.
- (d) Avoid salting or seasoning the fried food over the frier. They can accelerate the breakdown of the fat.
- (e) Lower the temperature when not frying and protect the fat from light.
- (f) The frying equipment should have no iron, copper or brass parts that come in contact with the heated fat.
- (g) Use a separate frier, if possible, for frying potatoes. The fat deteriorates more rapidly when meat or fish is fried than when only potatoes are fried.

The purpose of these guidelines was to encourage employees in food outlets to prepare high quality fried foods. The National Food Administration recommends the use of the Oxifrit Test as a quick test by kitchen staff and by the local food control inspectors and the method for the determination of total polar compounds is used as a reference method. In Sweden, antifoam agents, such as silicones, are not permitted in frying oils and fats because they mask the natural foaming in deteriorated fats and oils.

#### **2.2.17 Regulation on Frying Fats and Oils in Switzerland**

The Swiss Food Ordinance controls frying fats and oils in restaurants and catering facilities and give guidelines for food preparation and sale. The use of silicone additives in frying oils are forbidden. The food inspectors check frying

oils for odour, taste, colour and smoking and observe the state of hygiene in the food establishments.

The suspect frying oil quality is checked on the spot by the Fritest. If the result shows that the oil is deteriorated, the oil is taken to the laboratory and tested for the concentration of total polar compounds. A frying oil is considered to be deteriorated if :-

- (a) The odour and taste are extremely objectionable.
- (b) The smoke point is less than  $170^{\circ}\text{C}$ .
- (c) The total polar compound content is greater than 21% and the odour and taste are objectionable.
- (d) The total polar compound content is greater than 27% and the odour and taste are not clearly objectionable.

These criteria are based on the assumption that attention is given not only to the quality of the frying oil, but also to the hygienic condition of the kitchen.

### **2.2.18 Regulation on Frying Fats and Oils in U. S. of America**

Frying oils are subject to control under the general provisions of the Federal Food, Drug and Cosmetic Act, which states that a food is considered to be adulterated if it contains any poisonous substance which may render it harmful to health. The retail food protection code passed by The Food and Drug

Administration (FDA) contains a set of standards to assure hygienic practices and adequate operation and maintenance of equipment in food establishments.

The U. S. Department of Agriculture (USDA) have some general guidelines for frying meat and poultry products. The guidelines permit the addition of antioxidants and antifoaming agents in frying fats. The free fatty acid content in excess of 2,0% and large amounts of sediments are an indication that frying fats require replacement.

There are no specific regulations in U.S. cities and states other than those assuring that fats and oils used in food service establishment are obtained from approved sources and are not adulterated and the guidelines provided in Title 21 of the Code of Federal Regulations and the FDA Food Service Sanitation Manual of 1976.

The inspectors from The San Francisco Health Department check for colour, sediments, excessive smoke and odours of oils used in cooking and corrections are made through replacement of the cooking oils. Several states have now passed legislations requiring food establishments to inform customers of the type of frying oil used in preparation of foods and the percentage of saturated fat present in the frying oil.

Formal laws and regulations for the control of frying fat quality have been adopted by only a few countries. However, several other countries employ practical guidelines and test procedures to control the quality of frying fats, oils and fried foods. In addition, there is increasing awareness that good frying practice and proper control of frying fats improve the quality and acceptability of fried foods (Firestone, 1993).



## **2.3            RAPID ' ON THE SPOT ' QUALITY ASSESSMENT                  OF FRYING FATS AND OILS**

The quality of fried foods is affected by the quality of the frying fat or oil used. The German Society for Fat Science (GSFS) held two symposia on frying fats and oils in the 1970 's and following the second symposium in 1979 proposed that polar compounds be determined as a complement to the traditional organoleptic (sensory) evaluation of the quality of frying fats and oils. Many laboratory tests have been proposed for quality assessment of frying fats and oils.

A number of rapid "on the spot" test methods and kits, namely, the Oxifrit Test, the Fritest and the Veri-Fry Colorimeter Test, have become available, allowing inspectors and operators to easily test the frying fats and oils at the frier while the frying process is taking place.

### **2.3.1            The Oxifrit Test**

Frying fats and oils are deteriorated rapidly due to the presence of atmospheric oxygen, moisture and the high frying temperatures which causes physical and chemical changes to take place in the frying medium resulting in the formation of numerous and complex oxidation products which are collectively referred to as oxidised fatty acids.

The Oxifrit Test is a colour indicator test for the determination of oxidised fatty acids. After the test solution is added to the frying medium in a test tube and the mixture shaken, the colour changes to either blue, green or olive depending upon the amount of oxidised fatty acids present in the frying oil.

The results for this test are as follows :-

**BLUE COLOUR** - the oil is fresh and unused.

**GREEN COLOUR** - recommended that the oil needs to be changed.

**OLIVE COLOUR** - the oil is extremely deteriorated, unfit for further use and must definitely be discarded.

### 2.3.2 The Fritest

The Fritest is an "alkali colour number" indicator test to determine the concentrations of carbonyl compounds present in the frying medium. When an alkaline reagent is added to the frying medium the colour change is from Yellow when the test is performed on fresh, unused frying oil, to Brown when the test is performed on frying oil that is unfit for further use.

The standard colours are labelled numerically and when the colour of the test (frying oil) sample is compared against the corresponding colour of the standard sample an "alkali colour number" is obtained. The resulting number will determine the quality of the oil and whether the frying oil can be used further or discarded (Kock, 1994).

The standard colours have the following classification.

- COLOUR 1** - The quality of the frying oil is good and can be used further.
- COLOUR 2** - The quality of the oil is still acceptable as long as the taste of the fried food is acceptable.
- COLOUR 3** - The frying oil has deteriorated and recommended to be changed.
- COLOUR 4** - The frying oil is extremely deteriorated and unfit for further use.

### 2.3.3 The Veri-Fry Colorimeter Test

The Veri-Fry Colorimeter Test is a simple and rapid test which determines the Total Polar Materials present in the hot frying medium when the frying oil is mixed with a blue gel in a test tube and shaken to dissolve the blue gel and then placed in the colorimeter.

The reading from the colorimeter is the ' **action number** '. This reading will determine whether the frying oil should be used further or should be discarded, depending on the ' **action number** ' readings determined beforehand against a series of standards of known concentrations of Total Polar Materials for frying oils and fats established by the frying establishment (Firestone, 1993).

## 2.4 THE EFFECTS OF ANTIOXIDANTS ON FRYING FATS AND OILS

### 2.4.1 Natural Antioxidants

Antioxidants in the diet minimises lipid oxidation. Studies are being conducted on the role of  $\beta$ -carotene and vitamin C and E in inhibiting low density lipoprotein oxidation. Primary antioxidants such as vitamin E donate hydrogen to inactivate initial free radical, peroxy or hydroxy radicals. Carotenoids have been shown to quench free radical in membranes.

Consuming fruits and vegetables is a very healthy way to counteract the effects of lipid oxidation. The non-alcoholic phenol components of red wine can reduce the oxidation of low density lipoprotein in human. It is very important to have a variety of antioxidants in the diet from such sources as whole grain cereals, fruits and vegetables (Haumann, 1993).

A variety of mechanisms provides defences and protection against free radical damage to cells and tissues in the body (Table 2.2). Important antioxidants that can be synthesized readily within the body include Nicotinamide Adenine Dinucleotide Phosphate (NADPH) which is in the reduced form and Glutathione (GSH). However, these compounds are somewhat dependent on dietary intakes because niacin is required for the synthesis of NADPH and cystine for the

synthesis of GSH. Vitamin C (ascorbic acid) is an important antioxidant to quench oxyradicals in the body's aqueous components such as blood plasma and cell cytosol.

**Table 2.2**                      **Components of Antioxidant protection**

<u>Endogenous antioxidants</u>	<u>Dietary antioxidants</u>	<u>Metal-binding proteins</u>
NADPH and NADH	Vitamin C	Ceruloplasmin (Cu)
Glutathione and Thiols	Vitamin E	Metallothionein (Cu)
Ubiquinol (coenzyme Q)	Carotenoids	Albumin (Cu)
Uric acid	Polyphenols	Transferrin (Fe)
Bilirubin		Ferritin (Fe)
Metalloenzymes		Myoglobin (Fe)

Vitamin E (tocopherol) and ubiquinol (coenzyme Q) provide antioxidant protection in the body's lipid phases, especially protection of the unsaturated fatty acids of cell membranes. In addition to these antioxidants, certain metalloenzymes catalyze reactions which eliminate reactive oxyradicals. The three important enzymes are superoxide dismutase, catalase and glutathione peroxidase and the reactions they catalyze are shown in Table 2.3. The cytosolic form of superoxide dismutase requires zinc and copper, whereas the mitochondrial form requires manganese to neutralize the highly reactive superoxide radical anion.

The catalase enzyme requires iron for the removal of hydrogen peroxide. Glutathione peroxidase which uses GSH to destroy lipid peroxidases and

hydroperoxides, is presently the only selenoenzyme clearly established as essential for humans.

**Table 2.3 Free Radical scavenging enzymes**

<u>Enzymes</u>	<u>Reactions</u>
Superoxide dismutase	$2O_2^{\cdot -} + 2H^+ \longrightarrow H_2O_2 + O_2$
Catalase	$2H_2O_2 \longrightarrow 2H_2O + O_2$
Glutathione peroxidase	$ROOH + 2GSH \longrightarrow ROH + H_2O + GSSG$
GSH = reduced Glutathione      GSSG = oxidised Glutathione	

Hence, the essential trace metals mentioned are often classified as antioxidant nutrients. However, an overabundance of free metals, especially iron and copper, can catalyze oxidation of biomolecules. This is effectively prevented in the body by complexation of the metals with proteins such as transferrin and ferritin for iron and ceruloplasmin and metallothionein for copper (Jacob, 1994).

#### **2.4.2 Synthetic Antioxidants**

Common antioxidants including tocopherol, butylated hydroxyanisole (BHA), propyl galate (PG) and tertiary butylated hydroquinone (TBHQ) retard oxidation at ambient temperature, but they become substantially less effective or even inactive when subjected to elevated temperatures. They also tend to be lost through volatilization. The analysis of BHA and PG in the frying oil used to fry

potato sticks at 170° C was carried out. After four hours of frying, the initial concentration of 100 p.p.m. had fallen to around 10 p.p.m.

The addition of TBHQ and methyl silicone improved the performance of partially hydrogenated soyabean oil as a cooking medium. A mixture of dimethyl silixane, BHA and ascorbyl palmitate was used to improve the quality of the used oils which had been previously treated with bleaching clay. A combination of methyl silicone with citric acid and TBHQ have been used in one research study, whilst in another study a mixture of phenolic antioxidants with silicone and esters of ethylenediamine tetraacetic acid (EDTA) was used. Other antioxidants which have been tested for their effect on the stability of frying oils are polymeric antioxidants and spice antioxidants. Spice antioxidants are obtained from herbs which also contains flavonoids, citric acid, peptides and amino acids.

Silicones have been used to improve the stability of oils and fats during heating and frying. A concentration of 1 p.p.m. of methyl silicone in heated sunflower oil showed a significant protective effect in preventing oxidation. The addition of silicone in palm oil for frying prevents foaming and oxidation. The silicone also lengthens the shelf-life of the fried products as it forms a protective coating. Silicones have been found effective in suppressing thermal deterioration in other oils such as soyabean oil, butter oil, vegetable shortenings and salad oils.

The methyl silicone antioxidant forms a protective film at the air-oil interface which is supposed to act as an oxygen barrier. Investigations were also carried out on the use of dimethyl polysiloxane and this antioxidant improves the stability of the oil by effectively suppressing the thermal deterioration of the frying oil (Boskou).

### **2.4.3 The Role of Antioxidants on Heart Diseases**

A variety of evidence from animal and human studies suggests that antioxidant vitamins decrease the risk of developing coronary heart diseases. Oxidatively modified low density lipoprotein (LDL) leads to Macrophages that become engorged with lipid called "foam cells" which then initiate vascular fatty streaks and the atherosclerosis process. Evidence suggests that oxidised LDL may also contribute to atherosclerosis by other mechanisms such as toxicity and inhibition of the elastic response of vascular smooth muscles.

Studies on animals, primarily rabbits, show that atherosclerosis is reduced significantly by the addition of probucol, a synthetic antioxidant, to the diet and that this effect is independent of plasma cholesterol levels.

Oxidised LDL has been found in atherosclerotic plaques of humans and animals, and the presence of autoantibodies to oxidised LDL (the body's immunologic reaction to oxidised LDL) has been shown to correlate with the progression of



atherosclerosis. Dietary antioxidants may also reduce heart disease risk by improving lipid profiles and lowering blood pressure.

Increased vitamin C in the diet in particular has been linked with improved blood profiles of total and high density lipoprotein (HDL) cholesterol and with decreases in blood pressure. Vitamin C and E exert vasodialatory and anticlotting effects by altering the production of prostacyclin and other prostaglandins. Vitamin C is well known to be an important factor for maintenance of the elasticity of vascular tissues as it is an essential co-factor for molecular cross-linking of collagen.

Following the current dietary guidelines and health regulations which recommend decreasing the intake of fats and oils while increasing the intake of fruits and vegetables, there is a substantial increase in the intake of vitamin C, carotenoids and other photochemicals, such as flavonoids which are known to have antioxidant properties. An increase in the intake of antioxidants reduces the occurrence of heart diseases (Jacob, 1994).

## 2.5 KINETICS OF FAT PENETRATION IN FOODS

Deep fat frying is a rapid and easy process of cooking food mainly potato chips, fish and sausages. A great deal of refined fats and oils are used for this purpose, the most common ones are sunflower oil, groundnut oil, olive oil, hydrogenated coconut oil, shortening and lard. The function of the frying medium is to transfer the heat to the food.

In deep-fat frying the food is completely or almost completely immersed in hot oil or fat normally at temperatures over  $160^{\circ}\text{C}$ . In a food preparation establishment the oil or fat is used to prepare several batches of food. Many foods need a coating, such as batter, which sets when the food is placed into the hot oil or fat so that any loss of juices or absorption of lipids is kept to a minimum. Starchy foods and meat generally do not need a coating.

The result of deep fat frying produces foods with different structures, properties, textural changes, attractive and tasty surface, crust formation, increased palatability, browning reactions and chemical changes.

During deep-fat frying, the fat is continuously used at a high temperature in the presence of air and water. Oxidative transformation usually accompany and probably precede the thermal transformation of the frying medium. Intermittent

heating, similar to household frying, increases the degradation of the lipid probably owing to peroxide formation and decomposition products during the reheating, cooking and cooling cycles.

The chemical changes taking place in the frying medium are the result of the formation of many new decomposed chemical compounds. These decomposition products can be divided into two main classes, namely, volatile and non-volatile compounds. The volatile compounds are responsible for room odour during frying and the flavour of the deep fat fried foods.

Non-volatile compounds are formed simultaneously, both by thermal and oxidative mechanisms from the unsaturated fatty acids. The nature of the fat is also important ; unsaturated glycerides are more sensitive to the action of air and temperature. There is a slight difference between the chemical composition in the frying medium and the fat absorbed by the food after the frying process.

### **2.5.1 Structure of the Fried Food**

During deep fat frying, food loses water which is transformed into steam, a crust is formed with numerous cavities, pores and a larger surface area. The frying medium partly fills these cavities that are produced by the loss of water. The surface of the food has a crisp exterior layer produced by the dehydration of the outer layer of the food during the deep fat frying process. The formation of the

crisp exterior layer begins when the temperature of the frying fat or oil is about 100° C.

### **2.5.2 The absorption of Frying Fats and Oils in Fried Foods**

There are several factors that are responsible for the absorption of frying fats and oils in fried foods. These are :

- (a) The use of abused frying oils or fats.
- (b) The specific gravity and surface area of foods.
- (c) The temperature of the frying medium.
- (d) The viscosity of the frying medium.

#### **2.5.2.1 Abused Frying Fats and Oils**

The cooking or frying time of the food increases when abused frying oils or fats are used and this also increases the absorption of the frying medium into the fried food. This is due to the formation of a considerable amount of degraded products in the frying oils or fats.

#### **2.5.2.2 Specific Gravity and Surface Area of Foods**

The absorption of fat into the food decreases as the specific gravity of the food increases. The larger the surface area of the food that is in contact with the frying medium, the higher will be its fat content.

### **2.5.2.3 Temperature of Frying Medium**

The absorption of the frying medium in the fried food increases at a lower frying temperature and decreases at a higher frying temperature during the frying process

### **2.5.2.4 Viscosity of Frying Medium**

As the viscosity of the frying fat or oil increases during the frying process, the absorption of the frying medium in the food also increases. Autoxidation, thermal oxidation and polymerization of the frying fats and oils leads to the formation of degradation products causing an increase in the viscosity of the frying medium, which eventually leads to an increase in the absorption of the frying medium in the fried food (Guillaumin).

### **2.5.3 The Replacement Rate of Used Frying Fats And Oils**

Due to the ongoing absorption, the frying medium needs to be replaced on a regular basis. Whilst the high absorption rate of the frying oil or fat is undesirable and costly, a high replacement rate will ensure that the oil or fat never needs to be wasted.

Provided that the oil in use is in good condition, the addition of new oil will maintain and produce a good quality of fried foods. The replacement rate can be increased by :-

- (a) Increasing the production of fried foods.
- (b) Decreasing the size of the frying equipment.
- (c) Frying high absorption and low absorption foods  
in the same frying oil or fat.

The following formula is used to calculate the replacement rate and the result gives the percentage of oil being replaced, usually, on a daily basis.

$$R = \frac{N \times 100}{F}$$

where :  
R = Replacement Rate  
N = New Oil  
F = Frier Capacity

The minimum replacement rate should be 30% and it will not be necessary to discard the old oil if a replacement rate of 50% and over is achieved (Tongaat Oil Guide).

## 2.6 THE NUTRITIVE VALUE OF FRYING FATS AND OILS

Frying is a complex process in which many variables are at work, namely, the temperature of the frying medium, the length of time the frying lasts, the type of frying oil or fat used, the characteristics of the food, whether the frying fat or oil is heated intermittently or not, the degree of saturation or unsaturation of the fat or oil at the outset and the type of receptacle used for frying.

All of these variables, which are interrelated and occur simultaneously, in some way or the other affect the palatability and acceptability of the fats and oils. They also affect the digestibility and have an influence on growth and mortality and various aspects of lipid metabolism related to their intake. The opinion of a panel of tasters is very important when determining whether the fat or oil has deteriorated or not through repeated use from the taste and smell of the fried foods. However, under domestic conditions, the frying fat or oil is used up before a panel identifies or rejects the food fried in it. The consuming of deteriorated fats and oils used for frying has been defined as potentially toxic.

### 2.6.1 Palatability and Acceptability of Frying Fats and Oils

Factors such as taste, smell and texture are primarily decisive in the selection of dietary intake of fats and oils. The optimum degree of frying is determined by a concept of acceptability which is dictated by palatability tests and is a parameter

which depends on the type of food and fat or oil used and the conditions of frying.

The German Society of Fat Research has laid down that a fat or oil has deteriorated when a palatability panel considers that its smell and taste are not acceptable. The changes due to the degradation of a fat or oil affects its palatability more than its nutritive value. Oxidative and hydrolytic breakdown spoils the taste of a food even when only very small quantities of fats and oils are present in the fried food. In fact, the food becomes unpalatable before any other significant changes occur.

### **2.6.2 Changes of Fat Digestion produced by the Frying Process**

The absorption and digestion of fats are the two separate aspects of the process although they are often related. Absorption is the process whereby food substances pass from the small intestines to the internal medium, while the digestibility coefficient quantifies in total the percentage of ingested material that is absorbed and does not, therefore, appear in the faeces. It has been pointed out that there is an inverse relationship between the melting point of a fat and its digestibility provided the melting point is not more than 50° C.

The extent to which frying fats are polymerized is one of the principal factors behind their reduced digestibility. Polymerization affects the digestion of both



animal and vegetable fats and it must be remembered that the formation of polymers is confined to fats and oils which are heated above the temperatures reached in normal frying. The nutritive value of fats and oils decreases when they are heated to  $275^{\circ}\text{C}$  causing the fats to polymerize and also produce one or more dimer fatty acid radicals.

It must be mentioned that heating fats and oils at  $275^{\circ}\text{C}$  is definitely overheating and not frying under normal conditions. Catalytic hydrogenation of vegetable oils is used extensively to turn liquid oils into semi-solid fats which make it easier to convert them into margarines and shortenings. This partial hydrogenation decreases the polyunsaturated fatty acid content of the vegetable oils, improves their aromatic stability and makes them last longer in deep-fat frying. Studies have shown that the digestibility and absorption of hydrogenated fats and oils which are rich in *trans* fatty acids and used considerably in the food industry are the same as that of unhydrogenated fats and oils.

Researchers have highlighted the effect that the ingestion of fats and oils used in frying has on growth and weight variation compared to unused fats and oils. This effect depends on the condition under which the frying takes place, on the length of time the used frying fats are administered and on whether these fats are used as a whole or whether certain fractions of the fats which are believed to be toxic are used.

A reduction in dietary protein contributes to the effect that the ingestion of used frying fats and oils has on growth. The peroxidized linoleic acid reacts with the sulphur amino acids in proteins, thereby decreasing the digestive utilization of these oils which in turn may affect weight. Almost all amino acids react with primary and secondary products of oxidized lipids. Studies have shown that some shortening and fats used for frying may contain large amounts of *trans* fatty acids (Cuesta et al).

## 2.7 BIOLOGICAL EFFECTS OF DETERIORATED FRYING FATS AND OILS

It is commonly believed that fats subjected to high frying temperatures are dangerous to health. Fats and oils differ from each other in their fatty acids, mostly in the degree of unsaturation. Also of importance is the presence of certain minor component, among which the most interesting are the antioxidants.

A high degree of unsaturation makes fats more fluid, giving them also important biological properties, but, at the same time, making them more vulnerable to attack by atmospheric oxygen especially at high temperatures.

The degradation products are peroxides, aldehydes, ketones, hydroperoxides, polymers and cyclic monomers. Each of these compounds can cause toxic effects. Even though aldehydes and ketones, being volatile, are easily eliminated and the polymers are little absorbed, there are numerous experimental studies which may be relevant to man.

Many compounds are formed during frying, but, from a toxicological point of view, most interest is directed at the formation of peroxides. Antioxidants can reduce the thermo-oxidative deterioration, but it must be pointed out that the same heating reduces the antioxidant content, particularly the tocopherols.

### **2.7.1      The Absorption of Compounds from Used Frying Fats and Oils**

The study of intestinal absorption of compounds derived from the heating of fats and oils is of fundamental importance for evaluating their biological effects. Volatile substances, though important indicators of quality variation are lost and have no biological interest.

Studies conducted on non-volatile substances, with the canalization of the lymphatic duct, have shown that oxidised monomers are well absorbed, while the absorption of cyclic monomers is very high but polymers are very poorly absorbed. This observation is of very great clinical relevance because cyclic monomers are considered responsible for toxic effects and their formation seems to be proportional to the degree of unsaturation of the fat, as well as, to the time of exposure to high temperatures.

### **2.7.2      The effects of Compounds from Used Frying Fats and Oils on Vitamins**

Research have shown that frying, even for short periods, reduces the content of vitamin E. The degradation of vitamin E in the intestine is especially caused by the harmful substances produced during the oxidation of the frying fats or oils.

The destruction of vitamin E in membranes by peroxides or the subsequent free radical reaction is more important and rather serious.

### **2.7.3      The effects of Compounds from Used Frying Fats and Oils on Body Weight and Growth Rate**

The poor intestinal absorption of polymers and of heated fats and oils, in general, and the toxic effects caused by the degradation products are factors that result in loss of body weight and retard growth. Researchers conducted experiments on animals such as rabbits and rats and found that the ingestion of unused olive oil had no effect on body weight and growth rate, whereas the heated olive oil had a slight effect on body weight and growth rate.

However, the ingestion of either unused or heated sunflower oil and lard showed a greater deficiency in growth compared with olive oil. The ingestion of heated soybean oil and cotton seed oil resulted in a slightly reduced growth rate which was attributed to a decrease in the absorption of thermo-oxidized fats.

The ingestion of non-polar fractions from heated sunflower oil resulted in a reduction in the growth rate, while the ingestion of peroxidised and polymerized fractions of soybean oil showed a significant decrease in the growth rates as compared with the ingestion of fresh soybean oil.

#### **2.7.4      The effects of Compounds from Used Frying Fats                  and Oils on Stomach and Intestine**

Researchers have found that cooked fats and oils can cause stomach and intestinal problems which could lead to carcinoma, diarrhoea and the disturbance of the absorption of essential vitamins, proteins and carbohydrates.

#### **2.7.5      The effects of Compounds from Used Frying                  Fats and Oils on the Kidney**

The ingestion of thermo-oxidised fats and oils caused the kidney to increase in volume. This resulted in cellular degeneration, tubular necrosis and granular clumps that blocked the tubular lumen. Such lesions seemed more severe with rape seed oil, sunflower oil and lard than with olive oil in which case the damage observed was limited to an activation of the tubular epithelial cell nuclei. These effects, though very slight, were noted also with lightly re-heated frying oils.

#### **2.7.6      The effects of Compounds from Used Frying                  Fats and Oils on the Liver**

Studies have shown that, after heating, the more highly unsaturated fats and oils were responsible for greater liver damage than fats and oils of lesser unsaturation. This was confirmed when guinea pigs were fed with olive oil,

sunflower oil, butter and lard, after being heated at 170° C and aerated for one hour, resulted in the appearance of severe fatty livers with granulomatous areas and hyperplasia of Kupffer cells. All the fats under examination had this effect except for olive oil which caused only slight fatty degeneration.

Researchers conducted experiments on rats by feeding them with olive oil, rape seed oil, corn oil and lard, both unused and heated for 72 hours at 180° C. The results showed that with olive oil there were no necrotic zones but only a severe pyknosis of the nucleus with cytoplasmic atrophy, whereas, with thermo-oxidised rape seed oil and lard there were areas of necrosis and granulation with invasion by histocytes.

The liver reacts very differently in the case of fats cooked for a few hours, even at high temperatures, than it does when fats are cooked for a prolonged period. Researchers, having fed rats with fresh and heated sunflower oil and with polar and non-polar fractions of the used frying oil, observed a significant increase in liver weight with the polar fractions.

This was expected, considering the fact that the polar fraction contains the highest concentration of oxidation products. The polar fraction effected a significant increase in serum glutamic-oxidolacetic and glutamic-pyruvic transaminase.

Researchers studied the effect of cyclic dimers, trimers and monomers which were obtained from foods fried in soybean oil for 12 hours at 275° C under inert gas and noted modifications in hepatic lipids and an increase in serum alkaline phosphatase.

### **2.7.7        The effects of Compounds from Used Frying Fats                  and Oils on the Cardiovascular System**

Studies have demonstrated that ingestion of cooked fats increased the level of plasma cholesterol and of beta-lipoproteins. This effect seemed to be more evident with the use of animal fats, but it was also seen with sunflower oil which also caused a significant increase in the beta-lipoproteins. Researchers studied the synthesis of the prostaglandins at the platelets level and in the arterial intima checking the prostacyclin thromboxane balance known to be so important in determining thrombus and atheroma plaque formation.

The intake of heated poly-unsaturates, even with an adequate amount of Vitamin E, caused peroxidation, but most of all an increase of platelet thromboxane levels and a decrease of aortic prostacyclin, demonstrating how lipid peroxidation plays a highly important role in the synthesis of these eicosanoids and thereby, in the final analysis, in the determination of atherosclerosis.



Therefore, frying oils containing abundance of poly-unsaturates seem to represent, because of their easier peroxide deterioration, a risk factor for atherosclerotic disease.

Studies have shown that a massive calcification of the aorta's tunica media and sometimes even of the intima was due to the presence of polymers even though the fats contained sufficient essential fatty acids and vitamins and that these fats were not exposed to excessive heating.

It seems that fats and oils that have been heated, especially for long periods, seem to exert an atherogenic effect which appear more marked with the more highly unsaturated oils than with saturated fats. The modifications undergone by fatty materials with frying can, in some conditions, be responsible for physiological changes which can sometimes be severe.

The more notable effects are exerted by degradation products, namely the peroxides, hydroperoxides, the cyclic polymers and monomers derived mainly from the poly-unsaturated fatty acids, linoleic and linolenic acids. The presence of antioxidant agents can offer some protection, but because the oils and fats undergo extremely high temperatures there is also a decrease of the antioxidant levels due to the high frying temperatures (Viola and Bianchi).

The unsaturated fatty acids are more susceptible than saturated fatty acids to oxygen attacks during thermal oxidation and this results in the formation of *trans*-fatty acids and high concentration of polar compounds. *Trans*-fatty acids are the chemically altered form of the poly-unsaturates and studies have indicated that these *trans*-fatty acids are responsible for the increase in heart diseases and at one point was implicated as possible carcinogens (O' Brien, 1993).

Lipid oxidation has been found to influence the process of ageing and the onset of chronic diseases. Some of the breakdown products formed during the oxidation reaction are believed to be cytotoxic, carcinogenic or atherogenic. Cyclic fatty acids have been shown to cause toxicological effects with concentrations as low as 0,1% of the diet fed to rats. The consuming of highly oxidised foods have shown to cause harmful effects to health, nevertheless, it also would be of interest to study the effects of the volatile fat oxidation products that is inhaled by the people who operate the friers throughout the day.

Lipid oxidation causes inflammation in the body and is responsible for such diseases as arthritis, atherosclerosis, heart disease and breast and colon cancer. Free radicals of poly-unsaturated fatty acids can form in living systems, and oxygen can react with the radicals to form peroxy radicals and hydroperoxides. These compounds can chain react to cause membrane damage. In cardiovascular diseases, arterial clogging apparently begins when low-density lipoprotein (LDL) is oxidised in a reaction induced by free radicals.

The peroxidation of body tissues can disrupt membrane related functions, alter platelet functions, cause protein polymerization and promote atherogenesis by modifying LDL and cause Deoxyribonucleic Acid (DNA) mutation. However, the body has many protective mechanisms to control peroxidation and to quench, eliminate or inactivate free radical generations. These include enzymes such as superoxide dismutase, catalase, glutathione peroxidase, antioxidants and complementary agents such as ascorbic acid,  $\beta$ -carotene and retinoids. There have been evidence that dietary lipid oxidation products are involved in arterial injury, atherosclerotic plaque formation and thrombosis.

Consumption of rancid oils directly accelerates foam cell formation which causes atherogenesis. The absorption of cholesterol oxide indicates that cholesterol oxidation products found in the diet eventually ends up in plasma lipoproteins. The main sources of cholesterol oxidation products in the diet are obtained from foods that has been fried in animal fats.

Alternatively, researchers have found that lipid oxidation products can be used for therapeutic purposes. These oxidation products are capable of destroying cancer cells but not healthy and normal cells (Haumann, 1993).

The unsaturated fatty acids of lipids and lipoproteins are especially susceptible to free radical mediated oxidation and oxidative modification of LDL particles in

the blood is believed to be an important part of the atherosclerotic process. Lipid peroxidation has been suggested as a factor in degeneration of myelin, which are the fatty sheaths surrounding nerve tissues, in certain neurological diseases. Free radical damage to DNA is believed to play a role in the initiation of carcinogenesis. Oxy-radicals can also attack proteins, thereby changing their structure and ability to function (Jacob, 1994).

Formation of cataracts is believed to involve photolytic free radical mediated damage to protein in the lens which causes the lens to lose its transparency. However, lens tissues and the humors of the eye maintain high concentrations of vitamin C which is a natural oxygen and oxyradical scavenger.

Saturated fatty acids are least susceptible to oxidation but are known to be the most atherogenic due to hypercholesterolemia. Therefore, the human requirement for vitamin E increases with a higher poly-unsaturated fatty acid (PUFA) content in the diet (Jacob, 1994).

**Table 2.4**                      **Diseases and abnormal conditions associated with oxidant damage**

Ageing	Multiple sclerosis
Arthritis and inflammatory diseases	Neonatal lipoprotein oxidation
Atherosclerosis	Pancreatitis
Cancer	Parkinson's disease
Cataracts and macular degeneration	Pulmonary dysfunction
Diabetes	Renal diseases and haemodialysis
Drug reactions	Shock, trauma and ischemia
Inflammatory bowel diseases and colitis	

All of us need fat in our diet as a source of energy and to supply us with essential fatty acids and fat-soluble vitamins as well as for culinary reasons. Approximately 30 - 40% of our energy intake is derived from fat, most of which consists of triglycerides containing fatty acids with 16 and 18 carbon atoms. In the gastro-intestinal tract the dietary triglycerides are hydrolysed into monoglycerides, free fatty acids and glycerol before being absorbed in the intestines. Following re-esterification within the intestinal cells, the long chain triglycerides are incorporated in the chylomicrons and secreted into the blood via the lymphatic system.

Depending on the length of the carbon skeleton and on the number and the geometry of the double bonds, the different long chain fatty acids show different physiological properties. Although this presentation concerns the effects of variations of the type and amount of long chain fatty acids in the diet, the physiological effects of a change of dietary fat quality will also depend on several other factors, namely, the content of antioxidants in the diet, genetic predisposition and possibly gender.

A high saturated fat intake is correlated to elevated serum cholesterol concentration. This may be the major cause for the direct relationship between saturated fat in the diet and coronary heart disease. Researchers substituted dietary fat for carbohydrates to determine the effect of the dietary fat on the

serum lipoprotein composition. The concentrations of total cholesterol and low-density lipoprotein cholesterol increased considerably in the serum when saturated fat was substituted for carbohydrates in the diet, whereas, when unsaturated fat was substituted for carbohydrates the concentration of total cholesterol and low-density lipoprotein cholesterol were reduced. The reduction was more pronounced after poly-unsaturated rather than after mono-unsaturated fatty acids were substituted for carbohydrates.

The concentration of high-density lipoprotein (HDL) increases and the concentration of triglycerides decreases when dietary fat is substituted for carbohydrates, irrespective of the degree of saturation. The saturated fatty acids with 12, 14 and 16 carbon atoms are the major cholesterol elevating fatty acids.

Studies have shown that stearic acid with 18 carbon atoms did not seem to elevate the serum cholesterol concentration compared with carbohydrates or oleic acid. A comparison between a diet rich in stearic acid (18:0), a saturated fatty acid and a diet rich in linoleic acid (18:2 n-6), a poly-unsaturated fatty acid, however, showed that stearic acid caused an increase in total cholesterol and low-density lipoprotein cholesterol concentrations and a decrease in high-density lipoprotein cholesterol than linoleic acid in healthy people. The diets were identical except that 8% of the dietary fat was either stearic acid or linoleic acid.

Myristic acid (14:0), a saturated fatty acid, has shown to have the most pronounced cholesterol elevating properties while palmitic acid (16:0), a saturated fatty acid, increased the serum cholesterol concentration to a somewhat lesser extent. Lauric acid (12:0), a saturated fatty acid, increased the serum cholesterol and low-density lipoprotein cholesterol concentrations compared with oleic acid (18:1 n-9; *cis*), a monounsaturated fatty acid.

*Trans* isomers of oleic acid are formed during hydrogenation of linoleic acid or  $\alpha$ -linolenic acids (18:3 n-3) in the rumen of the cow or in the hardening factories of the industry. Elaidic acid (18:1 n-9; *trans*), a mono-unsaturated *trans* fatty acid have similar properties to those of saturated fatty acids than to the corresponding oleic acid which is also a mono-unsaturated fatty acid but in the *cis* configuration. However, the LDL cholesterol elevation caused by elaidic acid is less pronounced than that caused by the saturated fatty acid with 12-16 carbon atoms. An increase in the content of *trans* fatty acids in the diet seems to be associated with an increase of lipoprotein.

The immediate cause of acute coronary heart disease and sudden death is usually a thrombus formed at the endothelial surface of a ruptured atherosclerotic plaque or an episode of malignant cardiac arrhythmia. The long chain saturated fatty acids, including stearate, are more thrombogenic than linoleic acid.

Experimental research and clinical studies have shown that an anti-thrombogenic effect may be achieved by increasing the amount of n-3 fatty acids in the diet. The long chain poly-unsaturated fatty acids of the n-6 (arachidonic) and the n-3 (eicosapentanoic) series are precursors of the eicosanoids.

An increase in the concentration of the n-3 fatty acid has an effect on the cardiovascular system and contributes to the reduction of thrombus formation. The substitution of n-6 and n-3 fatty acids for saturated fat in the diet seems to reduce the frequency of cardiac arrhythmia. Addition of n-3 fatty acid in the diet of persons with mild hypertension has been associated with moderately reduced blood pressure levels.

Studies have shown that the dietary fat quality also affects the action of insulin. Insulin resistance is thought to be the major cause behind the development of different metabolic disorders, such as glucose intolerance and non-insulin dependent diabetes mellitus, essential hypertension, hypertriglyceridaemia and impaired fibrinolysis.

The majority of saturated fatty acids in the diet in descending order are palmitic, stearic, myristic and lauric acids. The cholesterol elevating saturated fatty acids with 12,14 and 16 carbon atoms constitute about 60-70% of all saturated fatty acids in the diet.

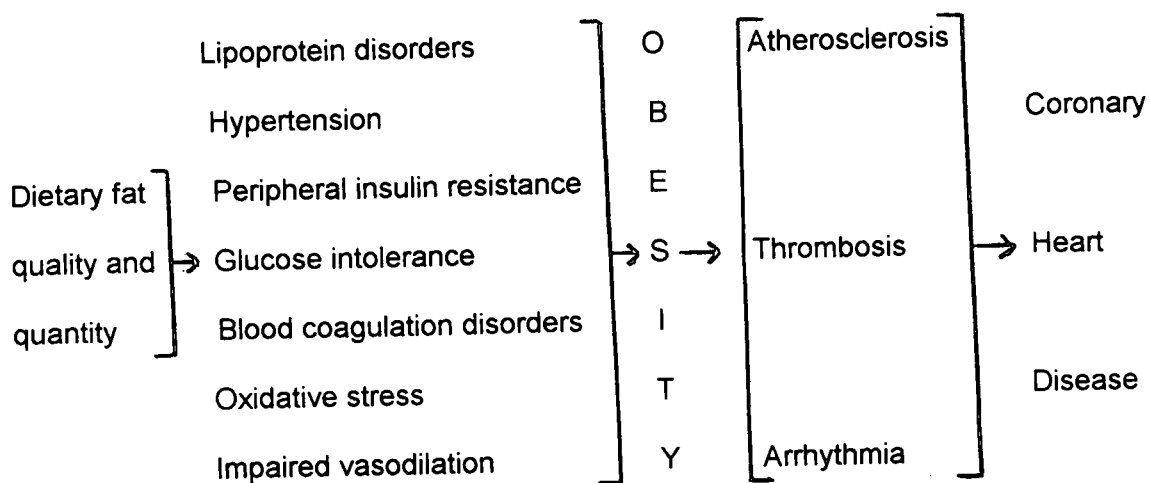


Meanwhile, researchers have found that clinical trials with garlic indicated that the equivalent of one-half to a clove of garlic a day lowered serum cholesterol levels by about 9% in persons with borderline-high and high cholesterol levels and this was due to alliin contained in the garlic as being responsible for the effect (Vessby, 1994).

**Table 2.5    The Effect of Dietary Fatty Acids on Serum Cholesterol levels**

<b>Fatty Acids</b>	<b>Effect on serum cholesterol when substituted for carbohydrates</b>
<b><u>Saturated</u></b>	
Caprylic (8:0)	neutral
Capric (10:0)	neutral
Lauric (12:0)	increase
Myristic (14:0)	increase considerably
Palmitic (16:0)	increase
Stearic (18:0)	neutral
<b><u>Mono-unsaturated</u></b>	
Oleic (18:1 n-9 ; cis)	decrease
Elaidic (18:1 n-9 ; trans)	increase
<b><u>Poly-unsaturated</u></b>	
Linoleic (18:2 n-6)	decrease
$\alpha$ -Linolenic (18:3 n-3)	decrease

**Table 2.6 Relationship between dietary fat and development of atherosclerotic cardiovascular diseases**



## **2.8 THE MANUFACTURING PROCESS OF VEGETABLE OILS**

There are two main processes, namely Expressing and Refining, that are involved in the manufacture of vegetable oils. These two processes are highly complicated and the utmost care and strict control is implemented during the various processing stages to obtain the finished product of the vegetable oils.

The Expressing process involves seed preparation and expelling and the Refining process involves neutralising, bleaching, winterising, deodorising, blending and packaging of the oil.

### **2.8.1 The Expressing Process**

#### **2.8.1.1 Seed Preparation**

The seeds are cut by fluted rollers into smaller pieces and prepared for the expelling process.

#### **2.8.1.2 Expelling**

The small seeds are squeezed through a screw type apparatus which forces the oil out of the seed and leaves behind the meal which is further processed into animal feeds. At this stage the crude oil, as it is known, has a strong odour and is dark in colour with the shade depending on the quality of the seed used. The crude oil is pumped into large storage tanks awaiting the refining process.

## **2.8.2 The Refining Process**

### **2.8.2.1 Neutralising**

The harmful acids, known as Free Fatty Acids, are removed from the crude oil. These acids cause the oil to deteriorate rapidly in storage and in use. The resulting by-product is known as acid oil and is used in the manufacture of soaps.

### **2.8.2.2 Bleaching**

The colour of the resulting oil will vary from batch to batch due to the different quality of the original seeds used. The refining process helps to overcome this, but in some cases the bleaching process is essential to obtain reasonably consistent colour levels. In some food preparations, especially mayonnaise and salad dressing, a lighter colour of oil is preferable.

### **2.8.2.3 Wintering**

This is a process where the waxes, which are a part of the oil seed, are removed. It is mainly the sunflower oil which is winterised and this process is carried out for appearance purposes. If an oil has not been winterised it will take on a milky appearance at low temperatures. This is caused by the waxes solidifying. It must be stressed that the performance of the oil is in no way affected and the milky colour disappears as soon as the oil is heated.

#### **2.8.2.4 Deodorising**

This process is extremely important in producing the best quality oil as the secret of good oil is that it does affect, in any way, the food being prepared.

This process removes any flavour or odour which the oil might have and results in a bland and odourless product. If the oil is not deodorised properly it will have a distinct rancid smell and this rancid smell will be evident in the food prepared in such an oil.

#### **2.8.2.5 Quality Control**

At this stage small samples of the refined oils from each batch are taken to the quality control laboratory and tested by qualified persons. Some of the tests performed are colour, free fatty acid content and smoke-point.

#### **2.8.2.6 Blending**

At this stage the refined oil is ready for blending if necessary. This is because some of the large food preparation establishments use an oil blend in the preparation of fried foods where two or three different oils; for example sunflower, groundnut, cotton seed, olive or palm oils; are blended by the oil manufacturer and supplied as requested.

#### **2.8.2.7 Packaging**

This is the final stage of the manufacturing process. The refined oils are packed into various sizes from a 750 millilitre , 2,5 and 5 litre plastic containers available at the supermarkets and grocery stores for the general public to the 25 litre plastic and the 205 litre steel containers for the medium and large food preparation establishments respectively (Tongaat Oil Guide).

## **CHAPTER 3**

### **3.0 MATERIALS AND METHODS**

#### **3.1 MATERIALS**

##### **3.1.1 Used Frying Fat and Oil Samples**

A total of twenty used frying fat and oil samples from both the formal and informal food frying outlets were collected by the environment health officer from the Durban Metro Health Department. The samples collected were from four different types of frying establishments, namely, five frying oil samples were from the hotels situated along the beach-front, five frying oil samples from the franchise outlets situated in the surrounding township, five frying oil samples from the restaurants situated in the Grey Street and Victoria Street Complex and five frying oil samples from the informal food frying outlets situated in the Warwick Avenue Bus and Taxi Terminal Complex.

All of these samples were collected from the friers, whilst the frying of the food was in progress, in separate 100g screw capped ointment bottles and, once received, were placed in a refridgerator to prevent any or further deterioration.

The brand names of the frying fats and oils used by these food frying establishments were helios and sunfoil oils and holsum shortening. A detailed information on the used frying fat and oil samples collected is listed in Table 3.1 and illustrated in Figures 6.7, 6.8, 6.9 and 6.10.

### **3.1.2 Unused Frying Fat and Oil Samples**

The unused helios and sunfoil frying oils, in 750 cm<sup>3</sup> plastic bottles, and a 250g block of holsum shortening were purchased from a nearby discount supermarket. These samples were also kept in the refridgerator.

### **3.1.3 Chemicals**

The Oil Reference Standard mixture of Fatty Acid Methyl Esters (FAME) AOCS No. 1 (CM1A) comprising of Palmitic Acid Methyl Ester (16:0) 6,0% ; Stearic Acid Methyl Ester (18:0) 3,0% ; Oleic Acid Methyl Ester (18:1) 35,0% ; Linoleic Acid Methyl Ester (18:2) 50,0% ; Linolenic Acid Methyl Ester (18:3) 3,0% ; Arachidic Acid Methyl Ester (20:0) 3,0% in N-Hexane and Oil Reference Standard mixture (FAME) NHI-D (CM2A) comprising of Myristic Acid Methyl Ester (14:0) 11,8% ; Palmitic Acid Methyl Ester (16:0) 25,6% ; Palmitoleic Acid Methyl Ester (16:1) 6,9% ; Stearic Acid Methyl Ester (18:0) 13,1% ; Oleic Acid Methyl Ester (18:1) 44,6% in N-Hexane were purchased from Sigma Chemicals, USA through Anatech.



The Silica Gel (70-230 mesh) Nr 7734 and the sea sand were purchased from E Merck. All other chemicals mentioned and used in this research project were of the AnalaR (AR) reagent grade purchased from Capital Enterprises.

#### **3.1.4 Glasswares**

The Chromatographic Glass Columns, 20 mm i.d. and 250 mm and 450 mm in lengths with teflon stop-cocks ; 250 cm<sup>3</sup> Dropping Funnels with ground glass joints and teflon stop-cocks and 250 cm<sup>3</sup> Receiving Flasks with ground glass joints and side arms were specially manufactured by and purchased from Mr. P Siegling. All other glassware used in this research project were the standard pyrex glassware, namely, beakers, measuring cylinders, pipettes and volumetric flasks of various sizes that are available in the Department of Chemical Sciences Chemistry Laboratories.

**Table 3.1 Information on the Used Frying Fat and Oil Samples**

<u>Sample number</u>	<u>Type of establishment</u>	<u>Brand name of Oil or Fat</u>	<u>Type of food fried</u>	<u>Usage of oil (days)</u>
1	Hotel	Helios	Chips	4
2	Hotel	Sunfoil	Chips	2
3	Hotel	Helios	Chips	3
4	Hotel	Helios	Chips	1
5	Hotel	Helios	Chips	1
6	Restaurant	Helios	Chips	7
7	Restaurant	Sunfoil	Chillie bites	2
8	Restaurant	Helios	Fish	1
9	Restaurant	Sunfoil	Chillie bites, peanuts	1
10	Restaurant	Sunfoil	Donuts	2
11	Franchise	Helios	Chips	4
12	Franchise	Holsum	Chicken	10
13	Franchise	Helios	Fish, Chips	4
14	Franchise	Helios	Chips	5
15	Franchise	Helios	Chips	2
16	Informal	Sunfoil	Liver, Sausages	3
17	Informal	Sunfoil	Liver, Sausages	1
18	Informal	Sunfoil	Chicken, Sausages	2
19	Informal	Sunfoil	Liver, Sausages	4
20	Informal	Sunfoil	Fish, Liver, Sausages	5

## **3.2 METHODS**

### **3.2.1 Qualitative Determination of Fatty Acid Methyl Esters (FAME)**

The Hewlett Packard 5890A Gas Chromatograph with the Chrom Perfect Chromatography Data System Computer Programme was used.

### **3.2.2 Determination of Refractive Index**

The Abbe Refractometer was used.

### **3.2.3 Determination of Viscosity**

The Brookfield Digital Viscometer with Spindle No. 3 was used.

### 3.2.4 The Determination of Free Fatty Acid and Acid Value Content in Used and Unused Frying Fats and Oils

The method of analysis was that followed as mentioned in the American Oil Chemists Society (AOCS) Official Method Ca 5a-40. Each sample was analyzed in duplicate. The frying fat and oil samples were massed, using an analytical balance, into a 250 cm<sup>3</sup> conical flask. 50 cm<sup>3</sup> of hot neutralized ethanol \* was added followed by 2 cm<sup>3</sup> of phenolphthalein indicator.

The solution was then titrated with standardised Sodium Hydroxide Solution (Appendix A), shaking the flask vigorously, to a permanent pink colour of the same intensity as that of the neutralized ethanol before the addition of the sample.

\*The neutralized ethanol was prepared by adding a few drops of phenolphthalein indicator to the ethanol and then titrating, very carefully, with the Sodium Hydroxide solution to a faint permanent pink colour just before use in the analysis of the samples.

### 3.2.5 Quantitative Separation of Monoglycerides, Diglycerides and Triglycerides by Silica Gel Column Chromatography

The analytical method was that followed as stated in the (AOCS) Official Method Cd 11c-93. The 20mm i.d. x 250mm in length glass column was prepared with 30g Merck Nr 7734 silica gel slurried in 60 cm<sup>3</sup> petroleum ether in a 100 cm<sup>3</sup> glass beakers.

The frying oil sample was massed into a 50 cm<sup>3</sup> glass beaker. About 3 cm<sup>3</sup> of chloroform was added to dissolve the sample and quantitatively transferred into the column. The beaker was rinsed with another about 3 cm<sup>3</sup> aliquot of chloroform and added to the column. The sample was eluted at a rate of 2 cm<sup>3</sup> min<sup>-1</sup> using 250 cm<sup>3</sup> of the appropriate solvent, for each fraction, placed in a 250 cm<sup>3</sup> dropping funnel attached to the top of the column into a clean, dry and pre-massed 250 cm<sup>3</sup> receiving flask attached to the bottom end of the column.

Fraction 1 (Triglycerides) was eluted by using 250 cm<sup>3</sup> of 10% Diethyl ether in Petroleum ether. Fraction 2 (Diglycerides) was eluted by using 250 cm<sup>3</sup> of 25% Diethyl ether in Petroleum ether. Fraction 3 (Monoglycerides) was eluted with 250 cm<sup>3</sup> of 100% Diethyl ether.

Each fraction was eluted into a separate receiving flask. After each complete elution, the receiving flask was placed on a steam water bath until the solvent was completely evaporated. The receiving flask containing the fraction was cooled to room temperature and then massed, placed back onto the steam water bath to remove more solvent if present, cooled and re-massed until a constant mass of the receiving flask was obtained.

### **3.2.6      Determination of Refractive Index of the Used and Unused Frying Fat and Oil Samples**

The analytical method was followed as described by the Association of Official Analytical Chemists (AOAC) Official Method of Analysis number 28.009 of 1984. The readings were determined at a temperature of 25°C using the Abbe Refractometer.

### **3.2.7      Determination of Peroxide Value of the Used and Unused Frying Fat and Oil Samples**

The analytical method was followed as described by the AOCS Official Method Cd 8-53. The analysis was determined in duplicate.

About 5.0g of the sample was massed into a 250 cm<sup>3</sup> conical flask with glass stopper. 30 cm<sup>3</sup> of a 3 : 2 acetic acid : chloroform solution was added into the

flask and swirled to dissolve the sample. Added  $0,5\text{ cm}^3$  of a saturated potassium iodide solution. Allowed the solution to stand with occasional shaking for 1 minute and then added  $30\text{ cm}^3$  of distilled water. The solution was titrated with the standardized Sodium Thiosulphate Solution (Appendix B) to a pale yellow colour.  $0,5\text{ cm}^3$  of the Starch indicator was added and the titration was continued until the colour changed from blue to colourless.

### **3.2.8        Determination of Polar and Non-polar Compounds in the Used and Unused Frying Fat and Oil Samples by Column Chromatography**

The analytical method was followed as described by the American Oil Chemists Society (AOCS) Official Method Cd 20-91

#### **3.2.8.1        Preparation of the Frying Fat and Oil Samples**

Between  $2,4\text{g}$  -  $2,6\text{g}$  of the sample was accurately massed into a  $50\text{ cm}^3$  volumetric flask. About  $20\text{ cm}^3$  of the elution solvent (87 : 13 Light petroleum ether : Diethyl ether) was added to dissolve the sample and then more elution solvent was added to the mark. Using a  $20\text{ cm}^3$  bulb pipette,  $20,00\text{ cm}^3$  of this solution was accurately pipetted into the prepared chromatographic column for analysis.

The solid frying fat sample was massed into a 50 cm<sup>3</sup> glass beaker. About 20cm<sup>3</sup> of the elution solvent was added to dissolve the fat and the solution was quantitatively transferred into the prepared column. More elution solvent was added to rinse the beaker and the rinse was also added into the column.

### **3.2.8.2 Preparation of the Chromatographic Column**

The glass column (20mm i.d. x 450mm in length with teflon stop-cock) was filled with 30 cm<sup>3</sup> of the elution solvent. A wad of cotton wool was introduced into the lower part of the column with the aid of a long glass rod and air was removed by pressing the wool.

About 25g of Merck Nr 7734 silica gel was massed into a 100 cm<sup>3</sup> glass beaker and about 80 cm<sup>3</sup> of the elution solvent was added to form a slurry. This silica gel slurry was poured into the column. The beaker was rinsed with more elution solvent and the rinse poured into the column to ensure complete transfer of the silica gel.

The silica gel was leveled by tapping against the column with a stainless steel spatula. About 4g of the sea sand was added into the column. The elution solvent was drained by opening the stop-cock until the level of the elution solvent reached the top of the sand layer.



### 3.2.8.3 The Elution of Polar and Non-polar Compounds

20,00 cm<sup>3</sup> of the oil sample solution was accurately pipetted into the prepared column using a 20 cm<sup>3</sup> bulb pipette. A clean, dry and pre-massed 250 cm<sup>3</sup> receiving flask was placed at the bottom end of the column. 150 cm<sup>3</sup> of the elution solvent was filled into a dropping funnel which was placed at the top end of the column.

The non-polar compounds were eluted first at a rate of 2,0 - 2,5 cm<sup>3</sup> min<sup>-1</sup> by adjusting the stop-cocks of the dropping funnel and the column. After the completion of the elution, a further 20 cm<sup>3</sup> of the elution solvent was added to wash any substance adhering to the outlet of the column and this washing was also collected in the receiving flask. The receiving flask was removed and placed onto a steam water bath to evaporate the solvent.

Another clean, dry and pre-massed receiving flask was attached to the bottom end of the column. 150 cm<sup>3</sup> of diethyl ether was filled into the dropping funnel and attached to the top end of the column. The polar compounds were eluted at the same rate as the non-polar compounds. After the completion of the elution, a further 20 cm<sup>3</sup> of diethyl ether was added into the column and eluted into the receiving flask.

The receiving flask was placed onto a steam water bath to evaporate the solvent. The flasks were cooled and then massed and the cooling and massing process repeated, until a constant mass was obtained, to determine the mass of the polar and non-polar compounds.

### **3.2.9 Qualitative Assessment of Column Efficiency by Thin Layer Chromatography (TLC)**

An approximately 10% in chloroform of both the eluted polar and non-polar compounds obtained from one of the frying oil samples by the above column chromatographic method was prepared separately. These prepared samples were spotted, using a capillary tube, about 10mm from the lower end of a 20cm x 20cm aluminium thin layer chromatographic (TLC) plate pre-coated with a thickness of 0,25mm of silica gel 60 without fluorescence indicator.

The developing solvent was 102 cm<sup>3</sup> of a mixture of light petroleum ether, diethyl ether and acetic acid in the ratio of 70 : 30 : 2 respectively and poured into a glass developing tank with a ground glass lid. Filter paper was placed on opposite sides of the inside of the tank to saturate the inner atmosphere of the tank. The spotted thin layer chromatographic plate was placed into the tank and developed for about one and half hours. The plate was removed and placed on a work bench for a few minutes to evaporate the developing solvent.

The plate was then sprayed with a 10% Phosphomolybdic Acid in ethanol solution in a fume cupboard and dried in an oven at 125 ° C for about 10 minutes. Figure 4,1 illustrates the chromatogram of the individual polar and non-polar compounds determined in the experiment and compares favourably with figure 4,2 from the AOCS Official Method Cd 20-91 confirming the efficiency of the Column Chromatographic Method.

### **3.2.10      Determination of Viscosity of the Used and Unused Frying Oil Samples**

The Brookfield Digital Viscometer was used to record the readings, in triplicate, using Spindle Number 3 at a speed of 100 rpm and a temperature of 26 ° C.

### **3.2.11      Qualitative Analysis of Fatty Acid Methyl Esters in Used and Unused Frying Fats and Oils by Capillary Gas Chromatography**

The frying fat and oil samples were, at first, converted to fatty acid methyl esters by following the (AOCS) Official Method Ce 2-66 (Appendix C) and an alternate method (Appendix D).

The analysis was determined by trial and error where different packed glass columns, packed stainless steel columns and capillary columns and changes in

column temperature and carrier gas flow rate were used in order to establish the optimum conditions where baseline separation of the fatty acid methyl esters (FAME) was achieved.

After several attempts, the following conditions and parameters were used to analyse the standards and the frying fat and oil samples.

**Instrument** : Hewlett Packard 5890A Gas Chromatograph  
Chrom Perfect Chromatography Data System

**Column** : Capillary Column No. 15064 Catalogue No. 2,4081  
Length 60 metres

**Range** : 2 x (3)

**Attenuation** : 2 x (2)

**Temperature** : Injector (B) 240 ° C  
Detector FID (A) 260 ° C  
Column (max) 225 ° C

**Gases** : Nitrogen 30cm<sup>3</sup> min<sup>-1</sup>  
Hydrogen 30cm<sup>3</sup> min<sup>-1</sup>  
Air 300cm<sup>3</sup> min<sup>-1</sup>

**Program** :

<u>Initial Temp</u>	<u>Hold</u>	<u>Rate</u>	<u>Final Temp</u>	<u>Final Temp Hold</u>
140 ° C	2 min.	10 ° C min <sup>-1</sup>	220 ° C	10 min.

**Split Ratio** : Flow 60 - 100 cm<sup>3</sup> min<sup>-1</sup>

**Signal** : About 23

## CHAPTER 4

### 4.0 CALCULATIONS AND RESULTS

#### 4.1 Determination of Free Fatty Acid and Acid Value Content in the Used and Unused Frying Fat and Oil Samples

The percentage of free fatty acid in majority of the frying fats and oils is calculated as oleic acid, although in coconut oil it is expressed as lauric acid and in palm oil it is expressed as palmitic acid.

The formula for the calculation of percentage free fatty acid and acid value according to the AOCS Official Method is as follows :-

$$(A) \text{ Percentage Free Fatty Acid} = \frac{\text{Titre volume (cm}^3\text{)} \times M \times 28.2}{\text{Mass of Sample (g)}}$$

where : M = Molarity of the Titrant (Sodium Hydroxide Solution)

$$(B) \text{ Acid Value} = \text{Percentage Free Fatty Acid (as Oleic Acid)} \times 1.99$$

The free fatty acids are frequently expressed in terms of acid value instead of percentage free fatty acid. The acid value is defined as the number of milligrams of Potassium Hydroxide necessary to neutralize 1g of sample.

By utilizing the formula, the percentage of free fatty acids as well as the acid values of the used and unused frying fat and oil samples, in terms of oleic acid, were calculated and is shown in Table 4.1.

**TABLE 4.1**      **Free Fatty Acid and Acid Value Content of Used and Unused Frying Fat and Oil Samples**

<u>Sample Number</u>	<u>Mass of Sample</u>	<u>Volume of NaOH</u>	<u>Mass of Sample</u>	<u>Volume of NaOH</u>	<u>Mean FFA</u>	<u>Acid Value</u>
	(g)	(cm <sup>3</sup> )	(g)	(cm <sup>3</sup> )	(%)	(%)
Helios	10,1313	0,25	11,7719	0,30	0,077	0,153
Sunfoil	10,0582	0,40	11,8909	0,45	0,120	0,239
Holsum	11,0701	0,20	12,9852	0,25	0,058	0,115
1	10,3085	2,75	10,4817	2,80	0,825	1,642
2	10,5018	1,35	10,2532	1,30	0,394	0,784
3	10,5098	5,90	10,7691	6,10	1,743	3,469
4	10,5038	0,35	10,6878	0,40	0,109	0,217
5	10,6484	0,70	10,4852	0,65	0,197	0,392
6	10,7089	1,85	10,4941	1,80	0,532	1,059
7	10,3469	0,45	10,6281	0,50	0,139	0,277
8	10,4872	0,40	10,7357	0,40	0,117	0,233
9	10,1974	1,15	10,3914	1,20	0,353	0,702
10	10,0712	0,85	10,2676	0,90	0,266	0,529
11	10,1402	0,90	10,3854	0,90	0,271	0,539
12	9,5328	6,50	10,0861	6,90	2,111	4,201
13	10,0287	3,10	10,2498	3,15	0,952	1,894
14	10,0574	5,40	10,1306	5,45	1,661	3,305
15	10,0240	2,60	10,1794	2,70	0,811	1,614
16	10,0169	5,25	10,1539	5,30	1,617	3,218
17	10,5415	3,15	10,7816	3,25	0,928	1,847
18	9,7037	3,30	10,0659	3,55	1,071	2,131
19	10,3615	4,20	10,5016	4,40	1,274	2,535
20	10,0153	2,90	10,2067	3,05	0,909	1,809

## 4.2 Quantitative Separation of Monoglycerides, Diglycerides and Triglycerides by Silica Gel Column Chromatography

The analyses were determined on randomly selected frying fat and oil samples.

The percent content of each fraction was determined by using the following general formula and are shown in tables 4.2 , 4.3 and 4.4.

$$\text{Percent Content of Fraction} = \frac{\text{Mass of Fraction (g)} \times 100}{\text{Mass of Sample (g)}}$$

**TABLE 4.2 Concentration of the Monoglyceride Fraction in Used and Unused Frying Fat and Oil Samples**

<u>Sample Number</u>	<u>Mass of Sample</u>	<u>Mass of Flask and Fraction</u>	<u>Mass of Flask</u>	<u>Mass of Fraction</u>	<u>Percent of Fraction</u>
	(g)	(g)	(g)	(g)	(%)
Helios	0,91	117,47	117,44	0,03	3,30
1	0,90	120,87	120,68	0,19	21,11
3	0,90	121,22	121,04	0,18	20,00
6	0,84	117,60	117,44	0,16	19,05
12	0,86	121,55	121,37	0,18	20,93
14	0,86	120,85	120,68	0,17	19,71
17	0,87	121,55	121,37	0,18	20,69
20	0,84	117,64	117,44	0,20	23,81

**TABLE 4.3 Concentration of Diglyceride Fraction in Used and Unused Frying Fat and Oil Samples**

<u>Sample Number</u>	<u>Mass of Sample</u> (g)	<u>Mass of Flask and Fraction</u> (g)	<u>Mass of Flask</u> (g)	<u>Mass of Fraction</u> (g)	<u>Percent of Fraction</u> (%)
Helios	0,91	121,42	121,36	0,06	6,59
1	0,90	121,06	121,04 <sup>6 1 5 6 1 5 2</sup>	0,02	2,22
3	0,90	117,45	117,44	0,01	1,11
6	0,84	121,39	121,37	0,02	2,38
12	0,86	120,71	120,68	0,03	3,49
14	0,86	121,07	121,04	0,03	3,49
17	0,87	120,70	120,68	0,02	2,30
20	0,84	121,38	121,37	0,01	1,19

**TABLE 4.4 Concentration of Triglyceride Fraction in Used and Unused Frying Fat and Oil Samples**

<u>Sample Number</u>	<u>Mass of Sample</u> (g)	<u>Mass of Flask and Fraction</u> (g)	<u>Mass of Flask</u> (g)	<u>Mass of Fraction</u> (g)	<u>Percent of Fraction</u> (%)
Helios	0,91	121,48	120,68	0,80	87,91
1	0,90	118,11	117,44	0,67	74,44
3	0,90	122,06	121,37	0,69	76,67
6	0,84	121,32	120,68	0,64	76,19
12	0,86	121,68	121,04	0,64	74,42
14	0,86	118,07	117,44	0,63	73,26
17	0,87	121,69	121,04	0,65	74,71
20	0,84	121,29	120,68	0,61	72 62



### 4.3 Determination of Refractive Index of the Used and Unused Frying Fat and Oil Samples

The Index of Refraction readings, for each sample, were determined in triplicate by approaching the intersection alternately from one field to the other, recording each reading, and then calculating the mean value. The Abbe Refractometer was used and the readings were determined at a temperature of 25 ° C and is listed in Table 4.5.

**TABLE 4.5            Refraction Index Values of Used and  
Unused Frying Fat and Oil Samples**

<u>Sample Number</u>	<u>Mean Values</u>
pure Helios oil	1,4711
pure Sunfoil oil	1,4710
pure Holsum	1,4783
1	1,4723
2	1,4729
3	1,4730
4	1,4720
5	1,4720
6	1,4723
7	1,4705
8	1,4719
9	1,4729
10	1,4722
11	1,4715
12	1,4825
13	1,4724
14	1,4725
15	1,4736
16	1,4729
17	1,4651
18	1,4658
19	1,4667
20	1,4714

#### 4.4 Determination of Peroxide Value of the Used and Unused Frying Fat and Oil Samples

The titration volume obtained for the blank sample was 00,00 cm<sup>3</sup> and the Molarity of the Sodium Thiosulphate Solution determined was 0,01005 mol dm<sup>-3</sup>.

The Peroxide Value for each sample was determined in duplicate, calculated by using the following formula and the readings and results are shown in Table 4.6.

Peroxide Value (millimoles of peroxide per 1000g of sample)

$$= \frac{(S - B) \times M \times 1000 (g)}{\text{Mass of Sample (g)}}$$

where :-

S = Titre volume for the Sample (cm<sup>3</sup>)

B = Titre volume for the Blank (cm<sup>3</sup>)

M = Molarity of Sodium Thiosulphate Solution (mmol cm<sup>-3</sup>)

**TABLE 4.6** Peroxide Values of the Used and Unused Frying Fat and Oil Samples

<u>Sample Number</u>	<u>Mass of Sample</u>	<u>Volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub></u>	<u>Mass of Sample</u>	<u>Volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub></u>	<u>Mean Peroxide Value</u>
	(g)	(cm <sup>3</sup> )	(g)	(cm <sup>3</sup> )	
Helios	5,1079	3,05	5,0273	2,95	5,949
Sunfoil	5,0967	3,50	5,1517	3,55	6,914
Holsum	5,7946	2,10	5,3471	1,95	3,654
1	5,0784	16,60	5,2107	17,10	32,916
2	5,1843	5,10	5,3846	5,30	9,890
3	5,0630	13,70	5,1021	13,85	27,238
4	5,0031	15,20	5,2437	15,90	30,504
5	5,0437	6,00	5,3091	6,30	11,941
6	5,0902	19,80	5,1187	19,95	39,132
7	5,0674	8,50	5,2305	8,75	16,835
8	5,0531	5,20	5,1729	5,35	10,368
9	5,0282	6,30	5,0906	6,40	12,614
10	5,0305	8,70	5,1928	9,00	17,400
11	5,0599	4,40	5,3509	4,60	8,690
12	3,6445	9,30	4,1897	10,75	25,716
13	5,0189	4,20	5,7069	4,70	8,344
14	5,0444	7,10	5,2835	7,50	14,206
15	5,0564	8,80	5,1992	9,00	17,444
16	5,2988	10,60	5,0587	10,20	20,185
17	5,0142	13,25	5,1653	13,70	26,607
18	5,1989	28,10	5,2263	28,30	54,370
19	5,1171	41,30	5,0997	41,10	81,055
20	5,1173	12,05	5,2859	12,50	23,716

#### 4.5 Determination of Polar and Non-polar Compounds in the Used and Unused Frying Fat and Oil Samples by Column Chromatography

The values of both the Polar and Non-polar compounds obtained in the experiment for Sample Number 16 was used as an example to illustrate the method of calculation and, by following the same method, the values and results of the other frying fat and oil samples were calculated and are shown in Tables 4.7, 4.8 and 4.9.

##### Calculation :

Mass of Oil taken = 2,5713g dissolved with elution solvent to  
the mark in a 50 cm<sup>3</sup> volumetric flask.

$$\begin{aligned}\text{Mass of oil in } 20,00 \text{ cm}^3 &= 2,5713\text{g} \times \frac{20 \text{ cm}^3}{50 \text{ cm}^3} \\ &= \underline{1,0285\text{g}}\end{aligned}$$

$$\begin{aligned}\text{Percent Polar Compounds} &= \frac{0,2633\text{g}}{1,0285\text{g}} \times 100 \\ &= \underline{25,60 \%^m/m}\end{aligned}$$

$$\begin{aligned}\text{Percent Non-polar Compounds} &= \frac{0,7638\text{g}}{1,0285\text{g}} \times 100 \\ &= \underline{74,26 \%^m/m}\end{aligned}$$

TABLE 4.7 Mass of Used and Unused Frying Fat and Oil Samples

<u>Sample Number</u>	<u>Mass of Oil</u>	<u>Mass of Oil</u> <u>in 20 cm<sup>3</sup></u>	<u>Mass of Fat</u>
	(g)	(g)	(g)
pure Helios oil	2,7044	1,0818	--
pure Sunfoil oil	2,5915	1,0366	--
pure Holsum	--	--	2,2398
1	2,5245	1,0098	--
2	2,6618	1,0647	--
3	2,5075	1,0030	--
4	2,6199	1,0480	--
5	2,5873	1,0349	--
6	2,5512	1,0205	--
7	2,5936	1,0374	--
8	2,5759	1,0304	--
9	2,6869	1,0748	--
10	2,5432	1,0173	--
11	2,6240	1,0496	--
12	2,4564	0,9826	--
13	2,8654	1,1462	--
14	2,6351	1,0540	--
15	2,5922	1,0369	--
16	2,5713	1,0285	--
17	--	--	1,5365
18	--	--	2,0797
19	--	--	1,9060
20	2,5084	1,0034	--

TABLE 4.8 Percentage of Polar Compounds

<u>Sample Number</u>	<u>Mass of Flask and Polar Compounds</u>	<u>Mass of Flask</u>	<u>Mass of Polar Compounds</u>	<u>Percentage of Polar Compounds</u>
	(g)	(g)	(g)	(%)
Helios	121,5857	121,5482	0,0375	3,47
Sunfoil	121,2977	121,2363	0,0614	5,92
Holsum	121,4601	121,2332	0,2269	10,13
1	121,1260	120,8671	0,2589	25,64
2	121,7299	121,5469	0,1830	17,19
3	121,8086	121,5692	0,2394	23,87
4	121,3233	121,2323	0,0910	8,68
5	121,6638	121,5492	0,1146	11,07
6	121,0946	120,8642	0,2304	22,58
7	121,6622	121,5531	0,1091	10,52
8	121,3252	121,2347	0,0905	8,78
9	121,6693	121,5529	0,1164	10,83
10	121,6725	121,5472	0,1253	12,32
11	121,4467	121,2320	0,2147	20,46
12	121,4699	121,2326	0,2373	24,15
13	121,8339	121,5477	0,2862	24,97
14	121,4936	121,2332	0,2604	24,71
15	121,4335	121,2340	0,1995	19,24
16	121,8122	121,5489	0,2633	25,60
17	118,0097	117,6253	0,3844	25,02
18	122,0912	121,5482	0,5430	26,11
19	121,7826	121,2320	0,5506	28,89
20	121,8018	121,5472	0,2546	25,37

TABLE 4.9 Percentage of Non-polar Compounds

<u>Sample Number</u>	<u>Mass of Flask and Non-polar Compounds</u>	<u>Mass of Flask</u>	<u>Mass of Non-polar Compounds</u>	<u>Percentage of Non-polar Compounds</u>
	(g)	(g)	(g)	(%)
Helios	121,9097	120,8663	1,0434	96,45
Sunfoil	118,5986	117,6246	0,9740	93,96
Holsum	119,6355	117,6270	2,0085	89,67
1	122,2871	121,5453	0,7418	73,46
2	121,7384	120,8663	0,8721	81,91
3	121,6226	120,8684	0,7542	75,19
4	118,5723	117,6247	0,9476	90,42
5	121,8744	120,8673	0,9171	88,62
6	122,3302	121,5500	0,7802	76,45
7	121,7818	120,8614	0,9204	88,72
8	118,5954	117,6643	0,9311	90,36
9	121,8054	120,8553	0,9501	88,40
10	121,7441	120,8609	0,8832	86,82
11	118,4509	117,6258	0,8251	78,61
12	118,3613	117,6251	0,7362	74,92
13	121,7145	120,8654	0,8491	74,08
14	118,4128	117,6259	0,7869	74,66
15	118,4516	117,6245	0,8271	79,77
16	121,6294	120,8656	0,7638	74,26
17	122,3812	121,2291	1,1521	74,98
18	122,4049	120,8682	1,5367	73,89
19	118,9794	117,6240	1,3554	71,11
20	121,6154	120,8680	0,7474	74,49

#### 4.6 Column Efficiency by Thin Layer Chromatography

Figure 4.1 illustrates the chromatogram obtained to assess the efficiency of the column by the T. L. C. Method.

#### 4.7 Determination of Viscosity of the Used and Unused Frying Oil Samples

The calculation of the viscosity, using a conversion factor of 10 and the mean value of three digital readings, of the used and unused frying oil samples was determined by applying the following formula and the results are shown in Table 4.10. The viscosity of the solid frying fat samples was not determined.

$$\text{Viscosity (centipoise)} = \text{Mean reading} \times \text{Conversion Factor}$$

**TABLE 4.10 Viscosity of the Used and Unused Frying Oil Samples**

<u>Sample Number</u>	<u>Mean Readings</u>	<u>Viscosity</u>
pure Helios oil	7,0	70
pure Sunfoil oil	7,3	73
1	9,1	91
2	7,5	75
3	7,6	76
4	8,2	82
5	7,4	74
6	8,0	80
7	7,9	79
8	7,6	76
9	7,6	76
10	7,5	75
11	8,9	89
12	solid	solid
13	7,9	79
14	8,4	84
15	9,3	93
16	10,6	106
17	solid	solid
18	solid	solid
19	solid	solid
20	8,2	82



#### **4.8            Qualitative Analysis of Fatty Acid Methyl Esters in Used and Unused Frying Fats and Oils by Capillary Gas Chromatography**

The Chromatograms (Figure 4.3 to Figure 4.26) show the presence of the different Fatty Acid Methyl Esters found in the Standard and the Used and Unused Frying Fat and Oil samples.

The Fatty Acid Methyl Ester components identified in the chromatograms were as follows:-

Myristic Acid Methyl Ester    (C14:0)

Palmitic Acid Methyl Ester    (C16:0)

Palmitoleic Acid Methyl Ester (C16:1)

Stearic Acid Methyl Ester    (C18:0)

Oleic Acid Methyl Ester       (C18:1)

Linoleic Acid Methyl Ester    (C18:2)

Linolenic Acid Methyl Ester   (C18:3)

Arachidic Acid Methyl Ester   (C20:0)

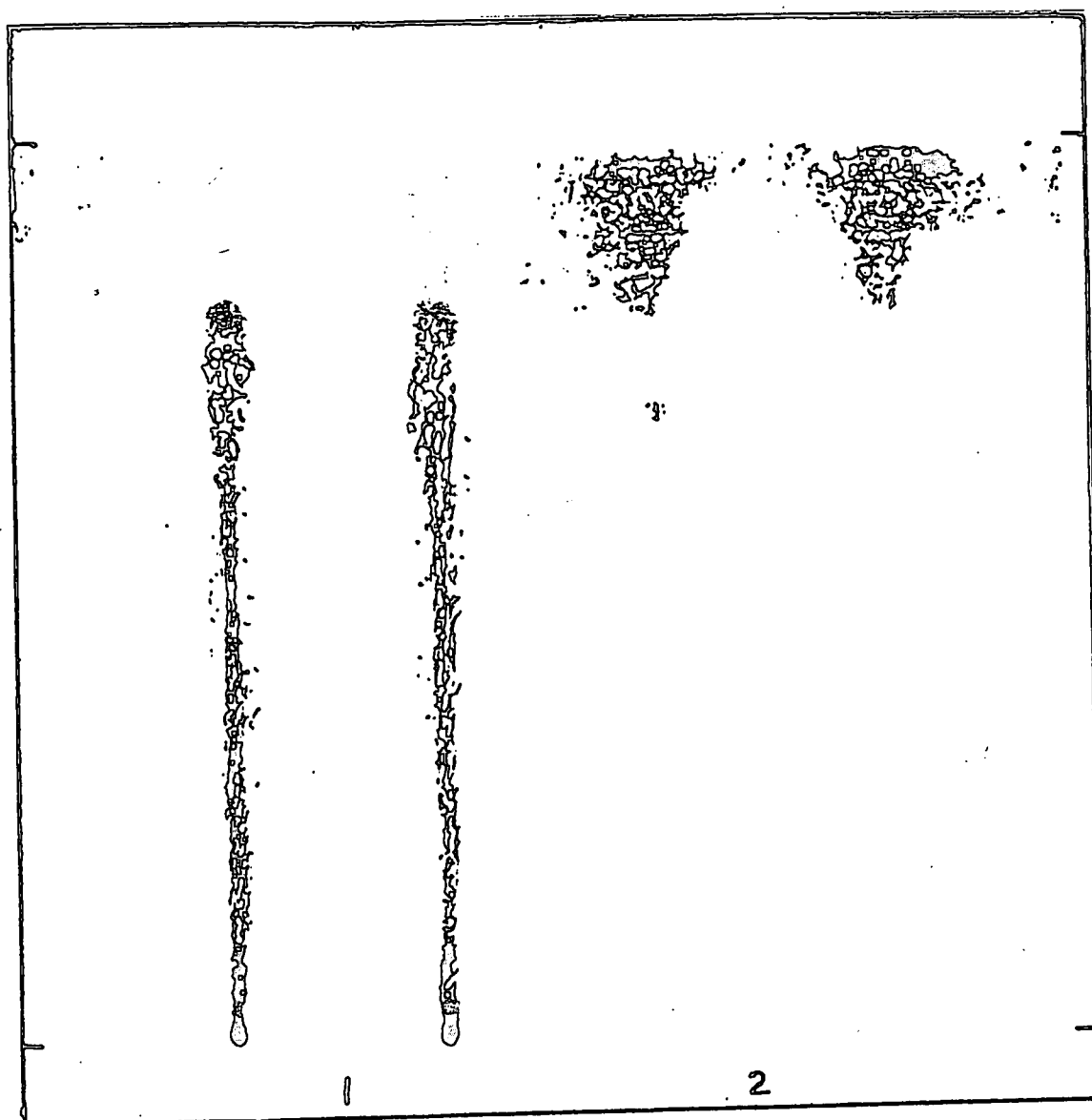


FIGURE 4.1  
CHROMATOGRAM SHOWING FRACTION 1 (POLAR COMPOUNDS) AND  
FRACTION 2 (NON-POLAR COMPOUNDS) OF A USED FRYING OIL SAMPLE

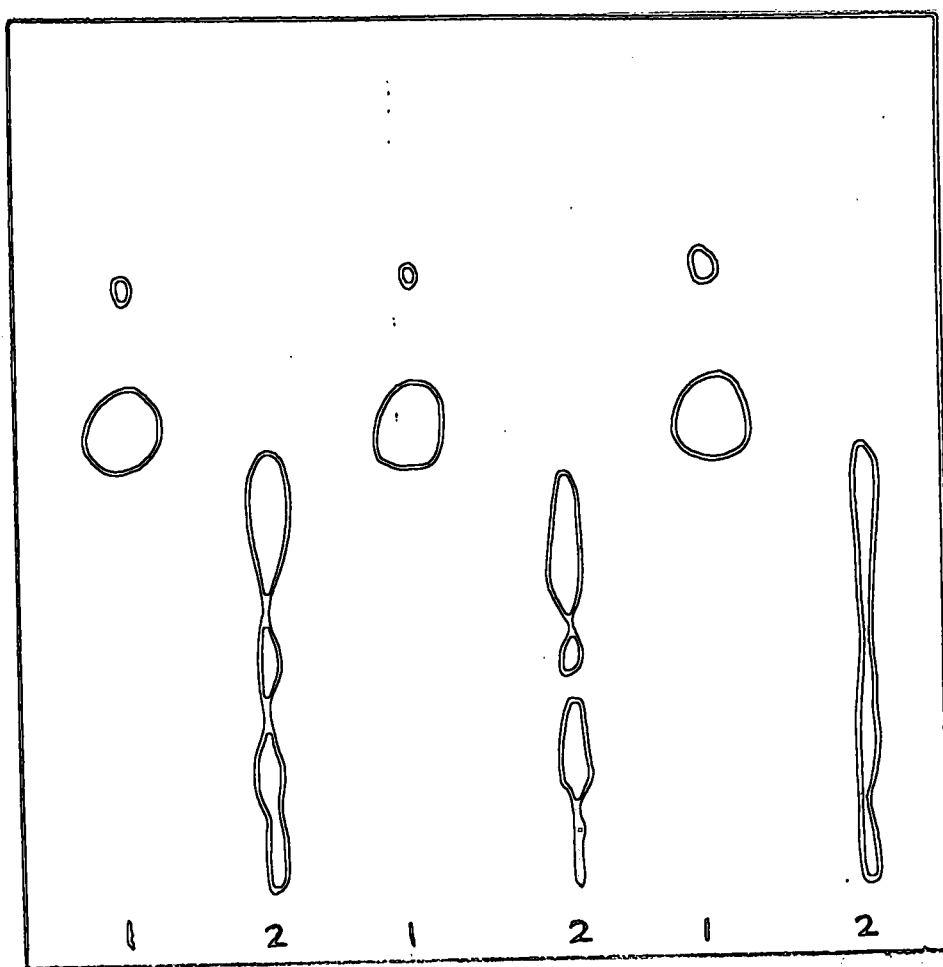


FIGURE 4.2  
CHROMATOGRAM SHOWING FRACTION 1 (NON-POLAR COMPOUNDS)  
AND FRACTION 2 (POLAR COMPOUNDS) OF A FRYING FAT SAMPLE

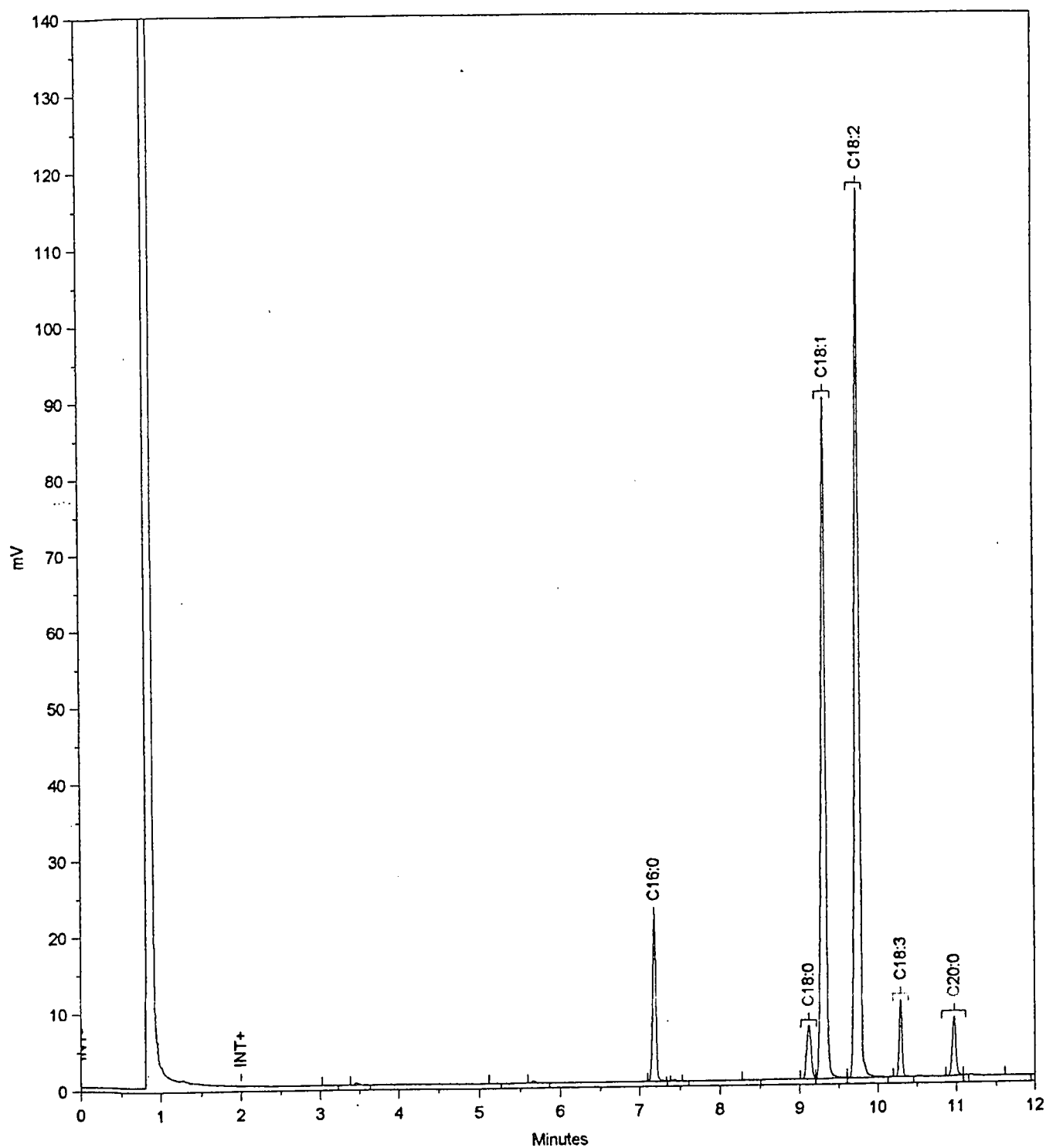


FIGURE 4.3  
CHROMATOGRAM OF FAME1.67R STANDARD SAMPLE (CM1A)

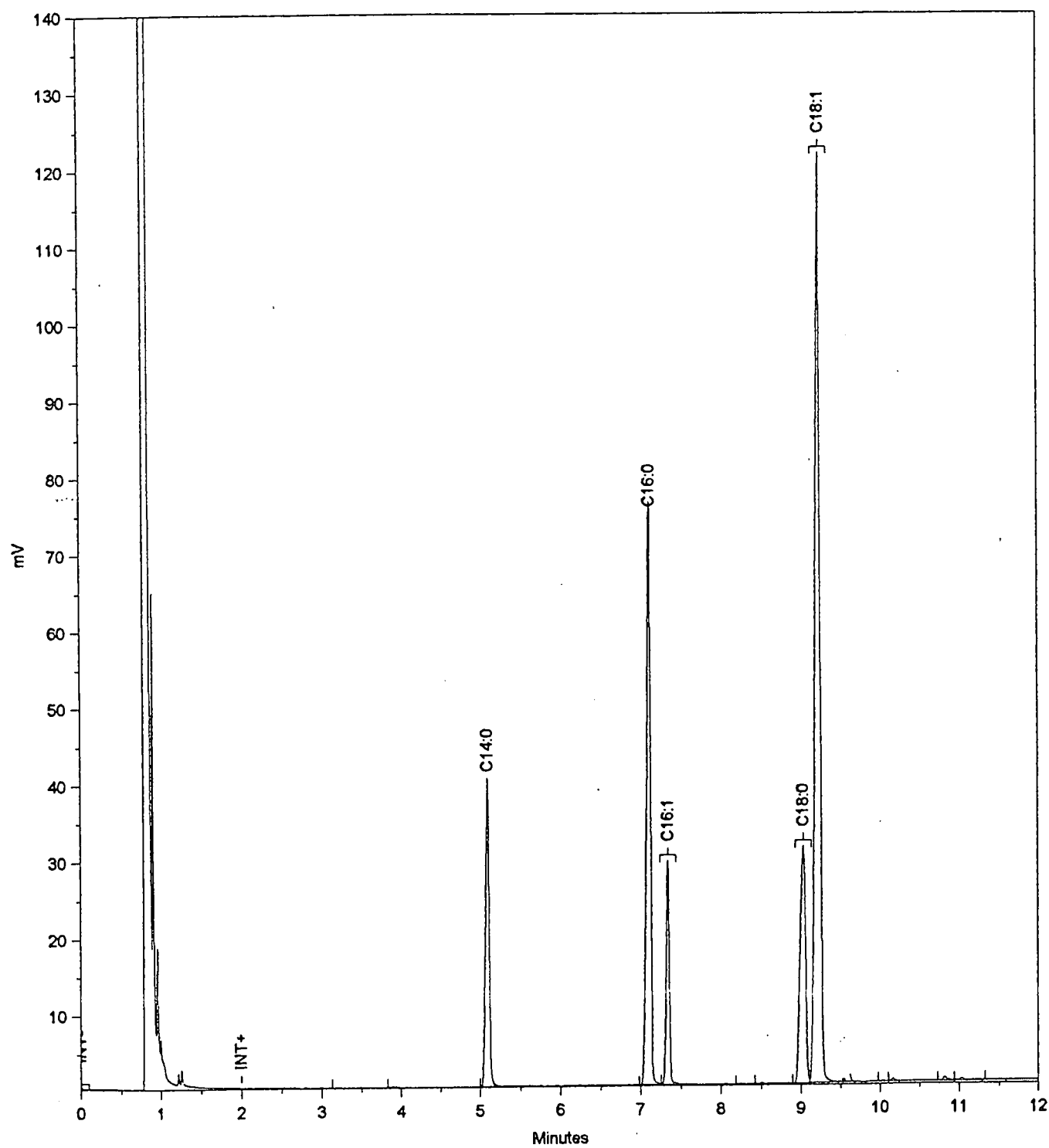


FIGURE 4.4  
CHROMATOGRAM OF FAME1.93R STANDARD SAMPLE (CM2A)

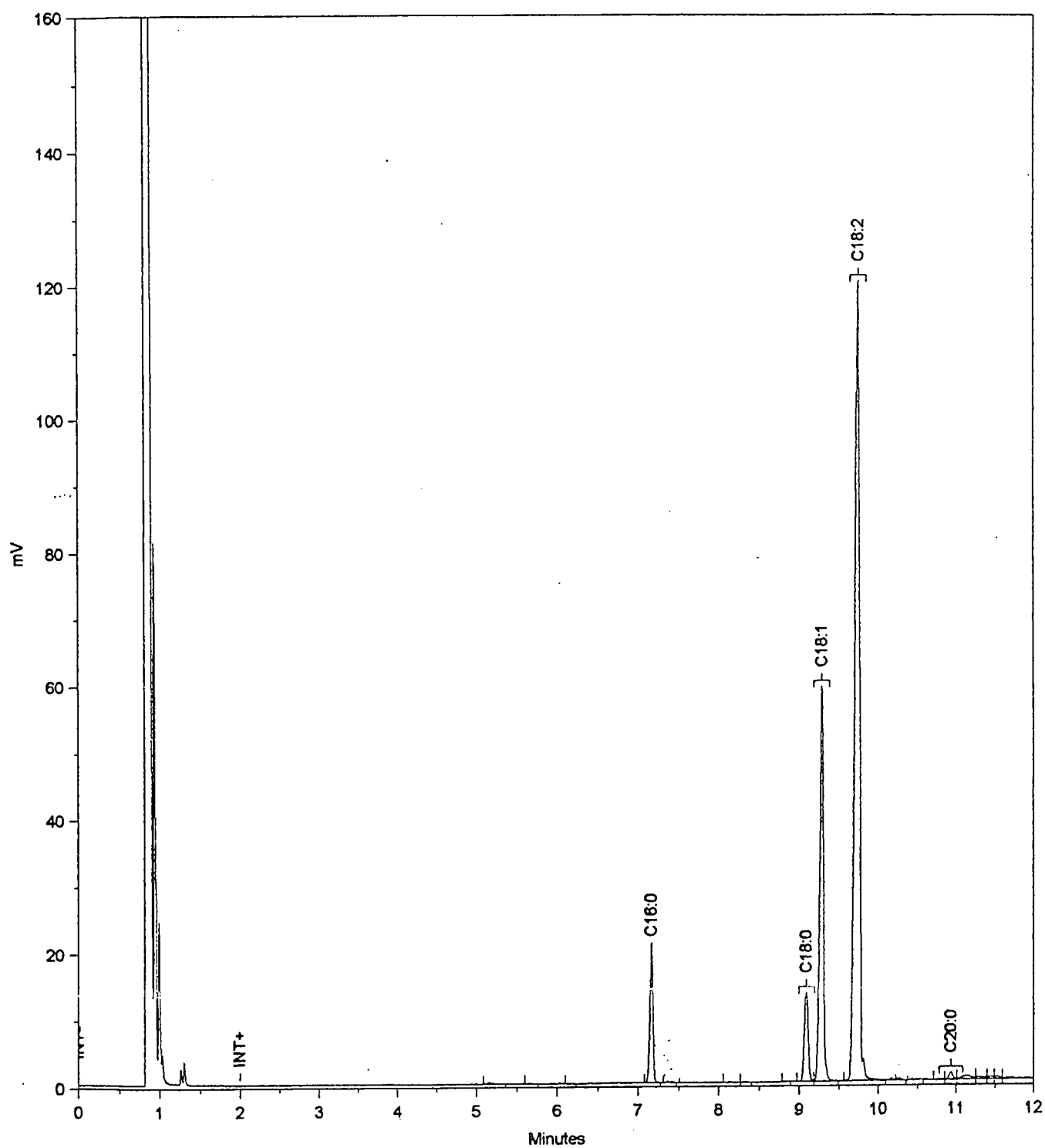


FIGURE 4.5  
CHROMATOGRAM OF FAME1.59R IN UNUSED HELIOS OIL (ALT)

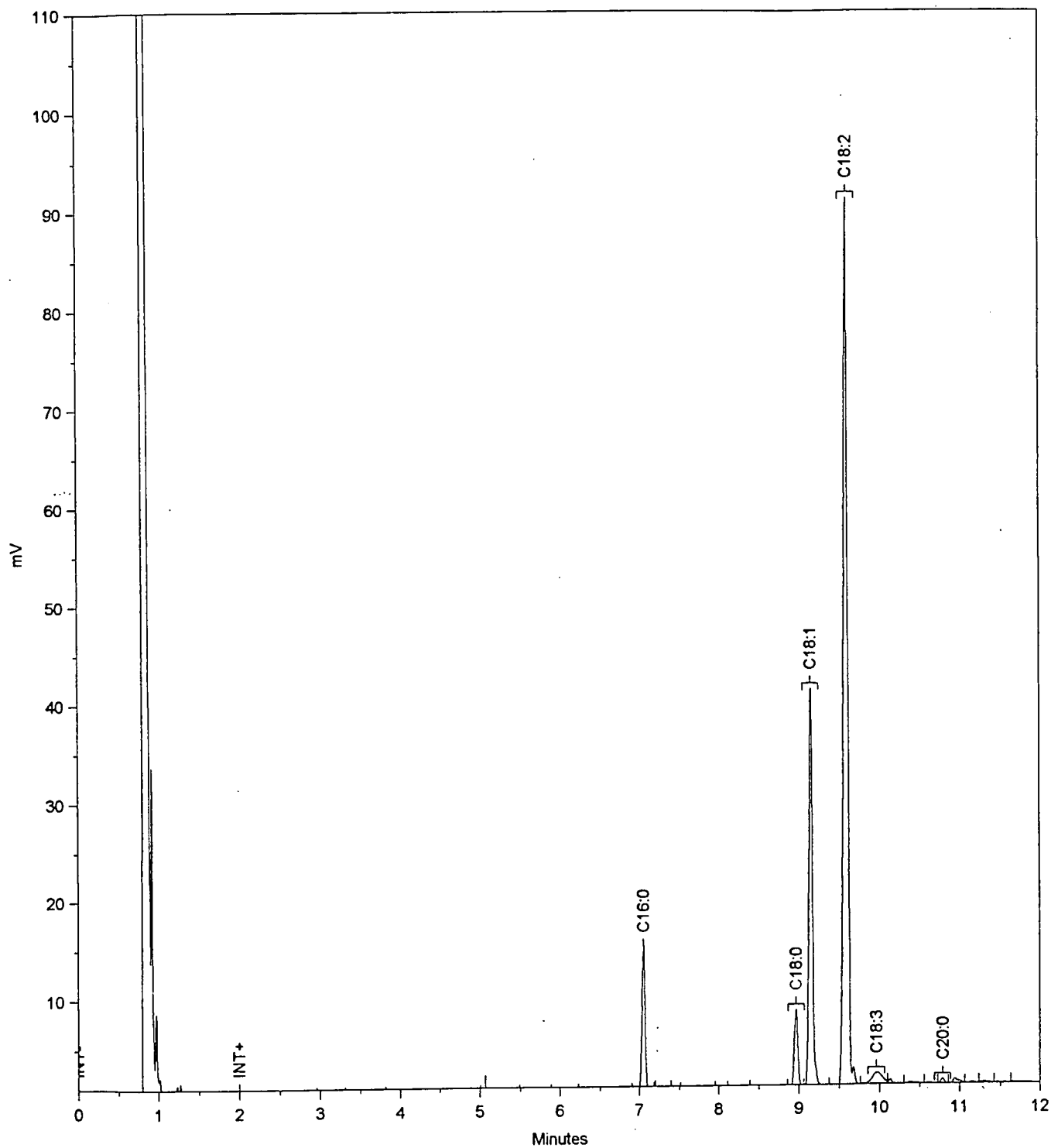


FIGURE 4.6  
CHROMATOGRAM OF FAME2.03R IN FRYING OIL SAMPLE 01 (AOCS)

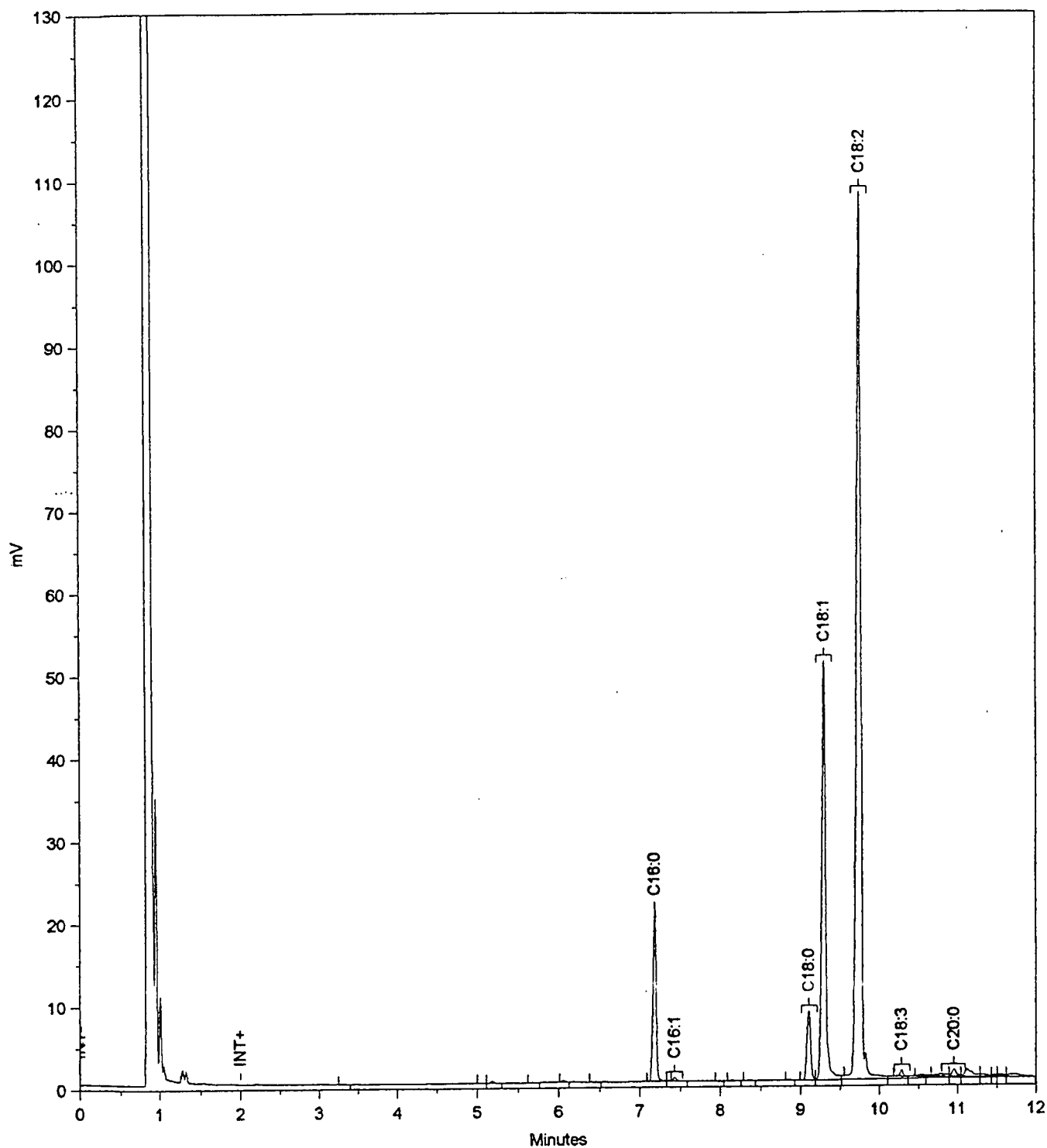


FIGURE 4.7  
CHROMATOGRAM OF FAME1.71R IN FRYING OIL SAMPLE 01 (ALT)



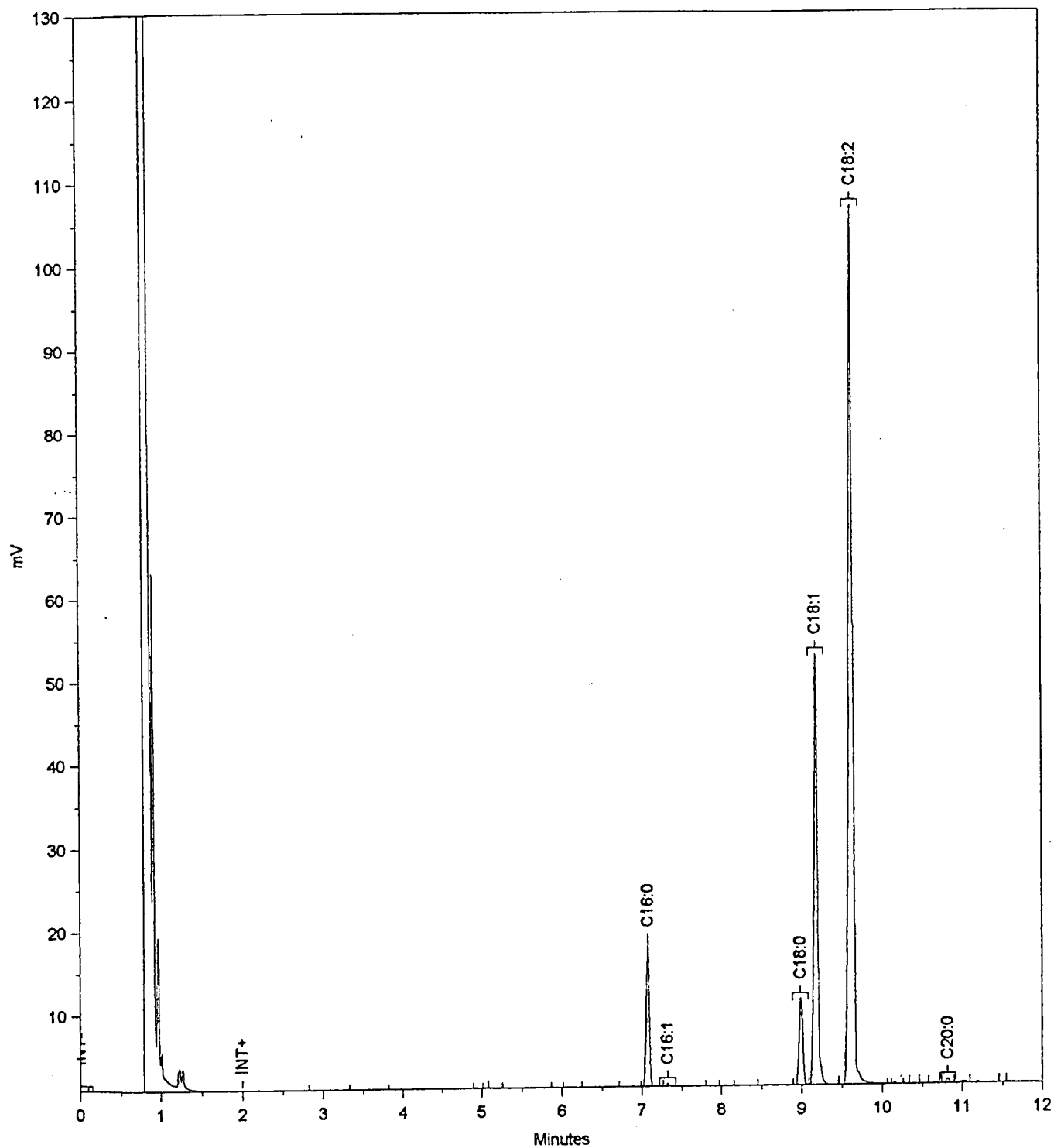


FIGURE 4.8  
CHROMATOGRAM OF FAME1.94R IN FRYING OIL SAMPLE 03 (AOCS)

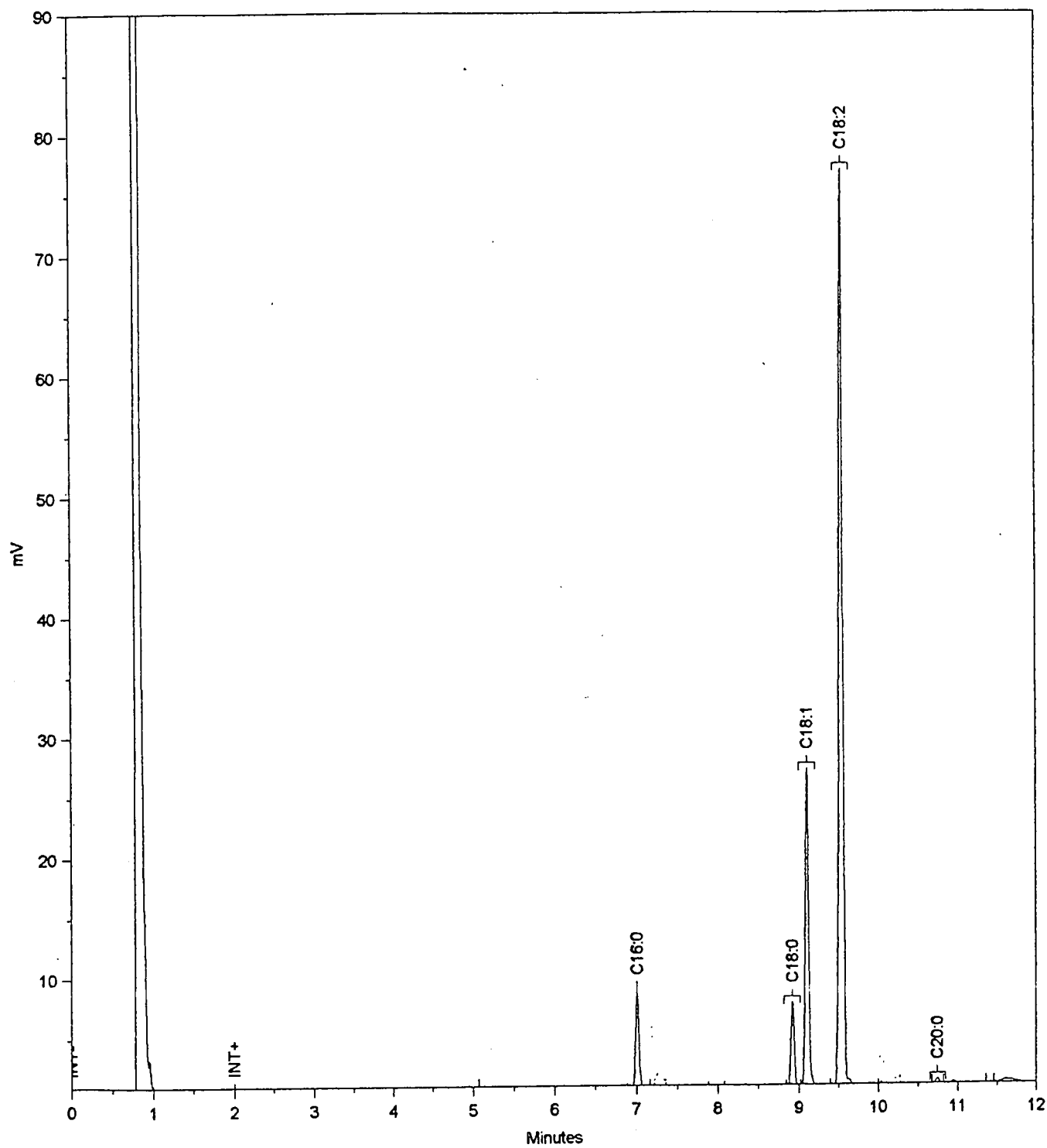


FIGURE 4.9  
CHROMATOGRAM OF FAME2.04R IN FRYING OIL SAMPLE 04 (AOCS)

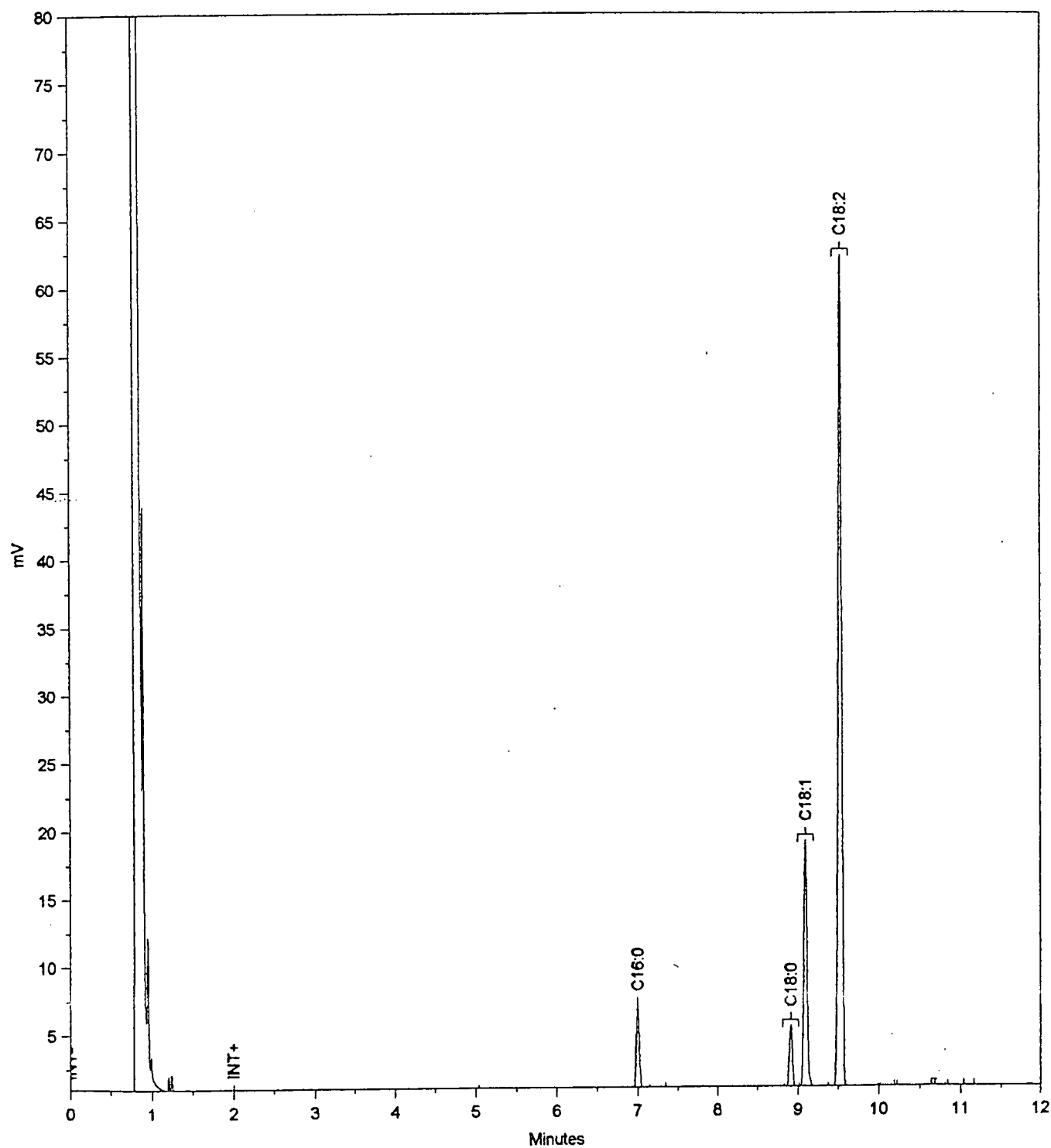


FIGURE 4.10  
CHROMATOGRAM OF FAME2.14R IN FRYING OIL SAMPLE 04 (ALT)

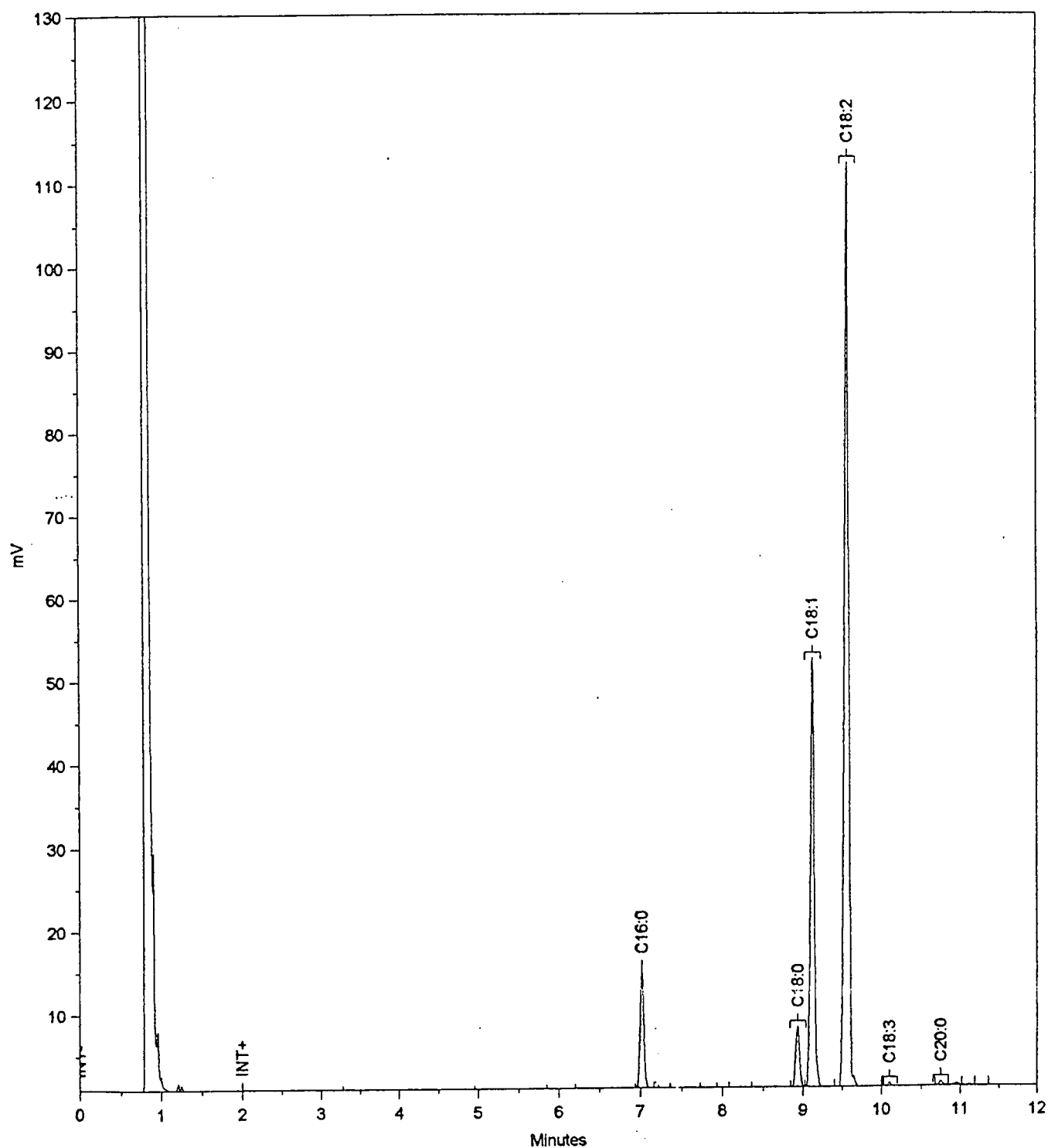


FIGURE 4.11  
CHROMATOGRAM OF FAME2.05R IN FRYING OIL SAMPLE 06 (AOCS)

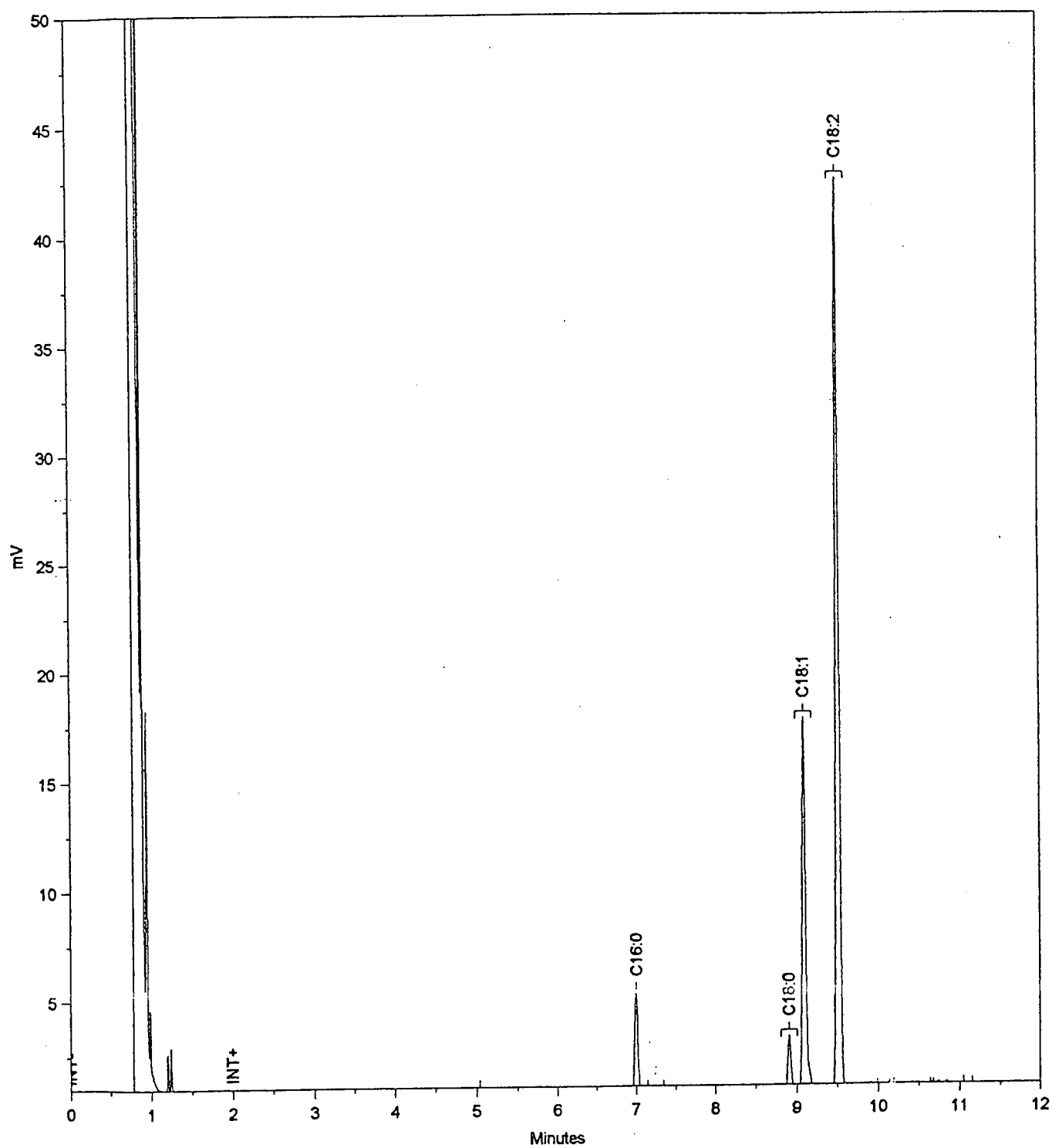


FIGURE 4.12  
CHROMATOGRAM OF FAME2.15R IN FRYING OIL SAMPLE 06 (ALT)

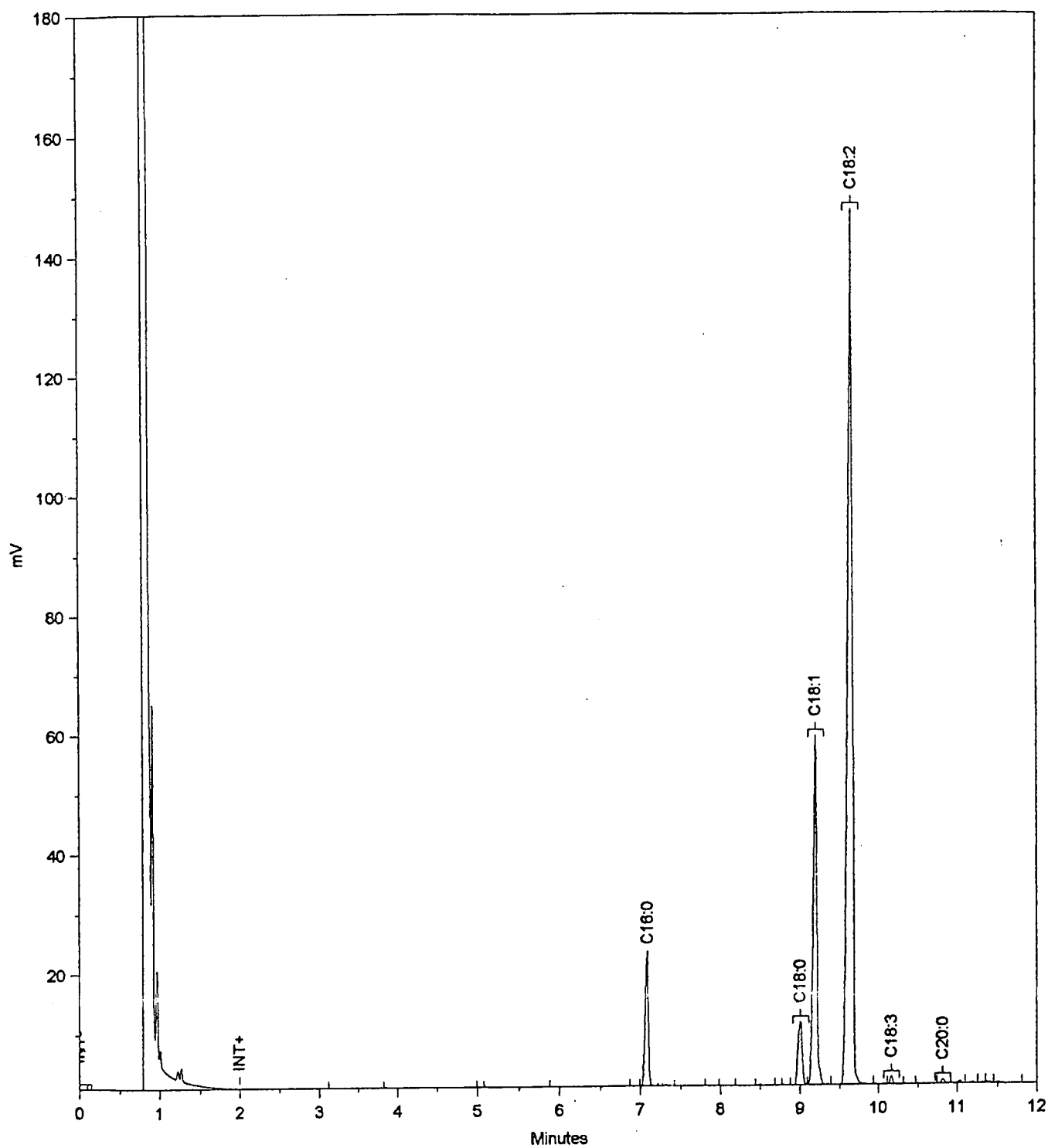


FIGURE 4.13  
CHROMATOGRAM OF FAME1.95R IN FRYING OIL SAMPLE 08 (AOCS)

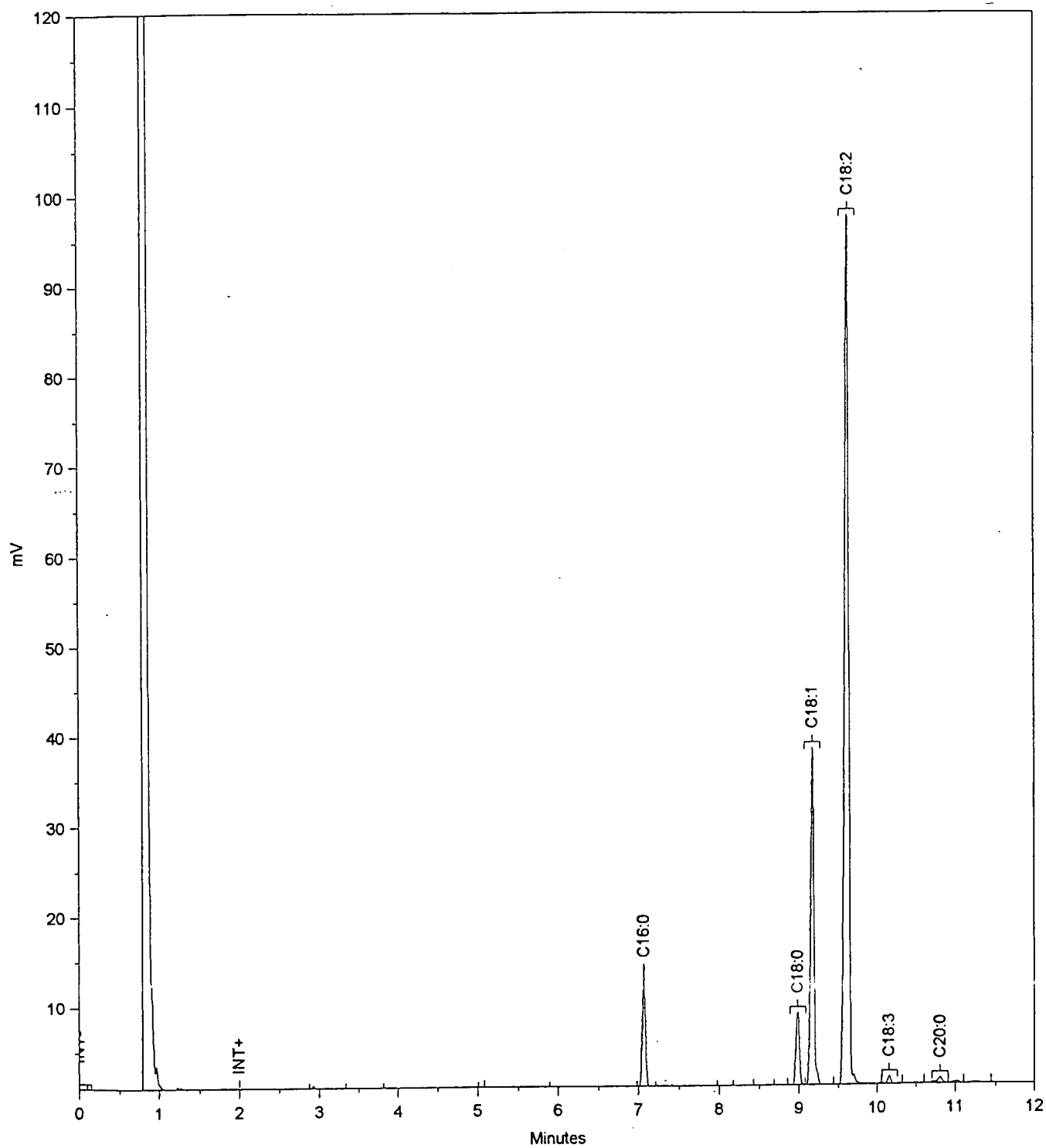


FIGURE 4.14  
CHROMATOGRAM OF FAME1.96R IN FRYING OIL SAMPLE 10 (AOCS)

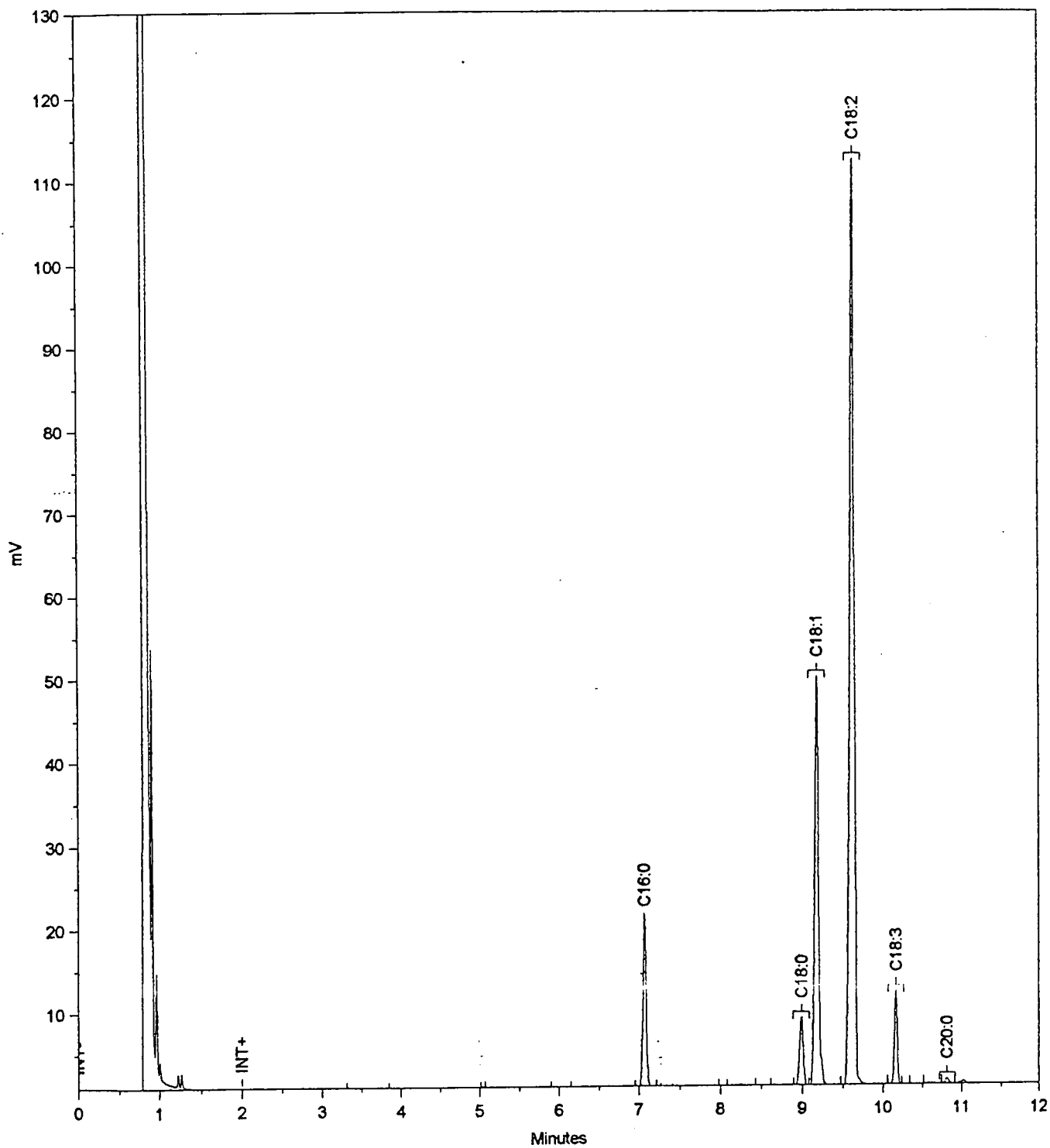


FIGURE 4.15  
CHROMATOGRAM OF FAME1.97R IN FRYING OIL SAMPLE 11 (AOCS)



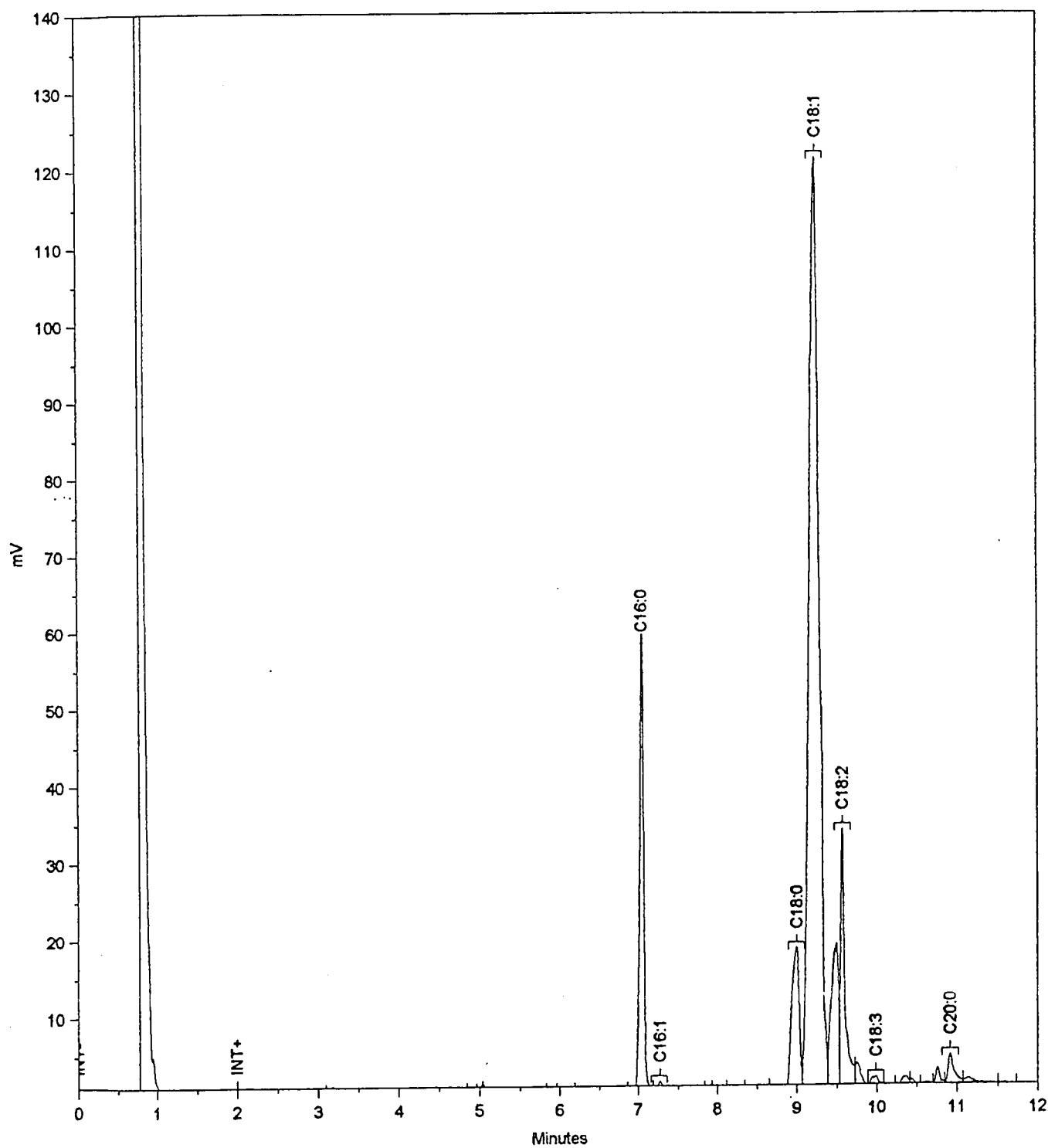


FIGURE 4.16  
CHROMATOGRAM OF FAME2.06R IN FRYING FAT SAMPLE 12 (AOCS)

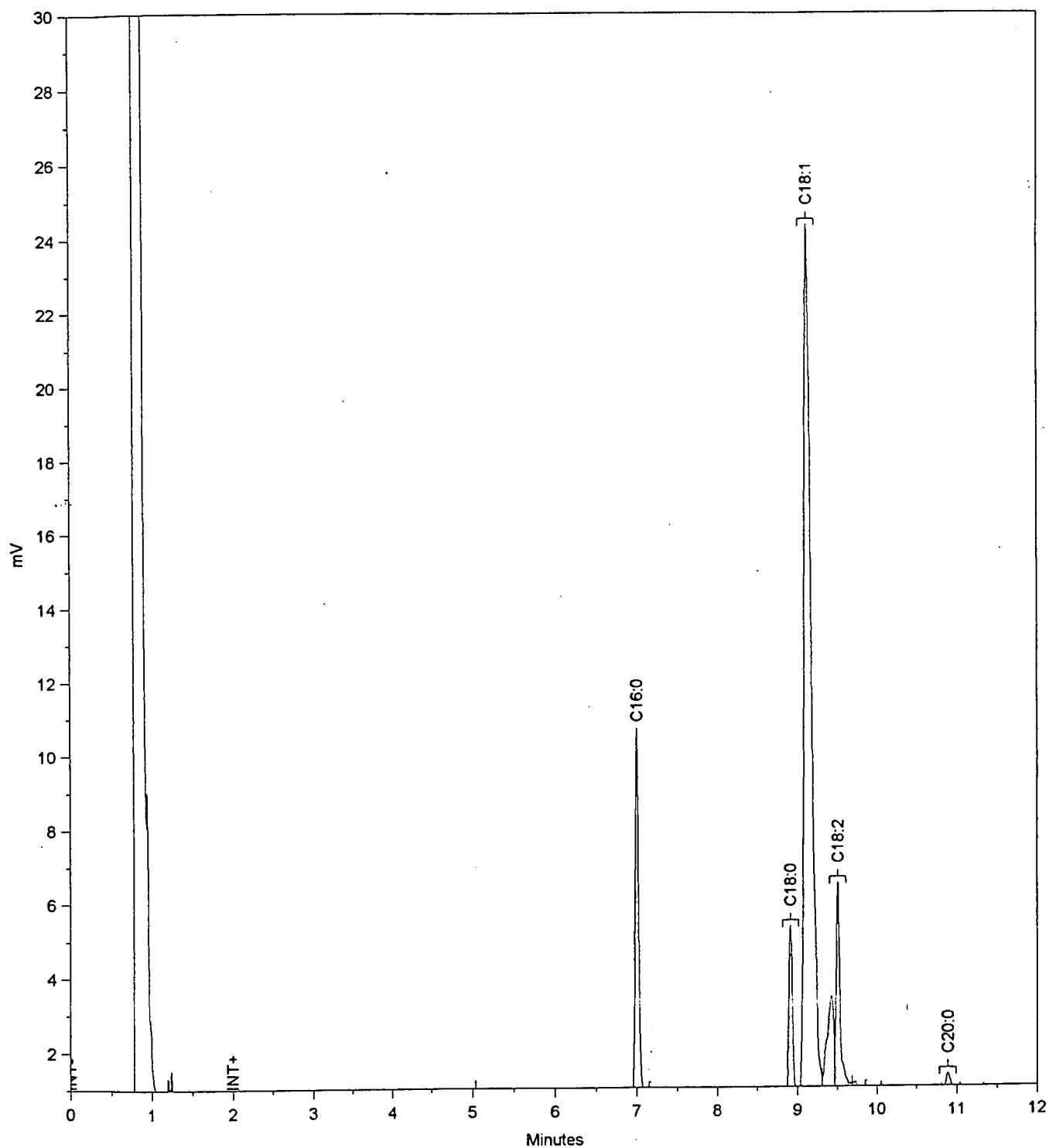


FIGURE 4.17  
CHROMATOGRAM OF FAME2.16R IN FRYING FAT SAMPLE 12 (ALT)

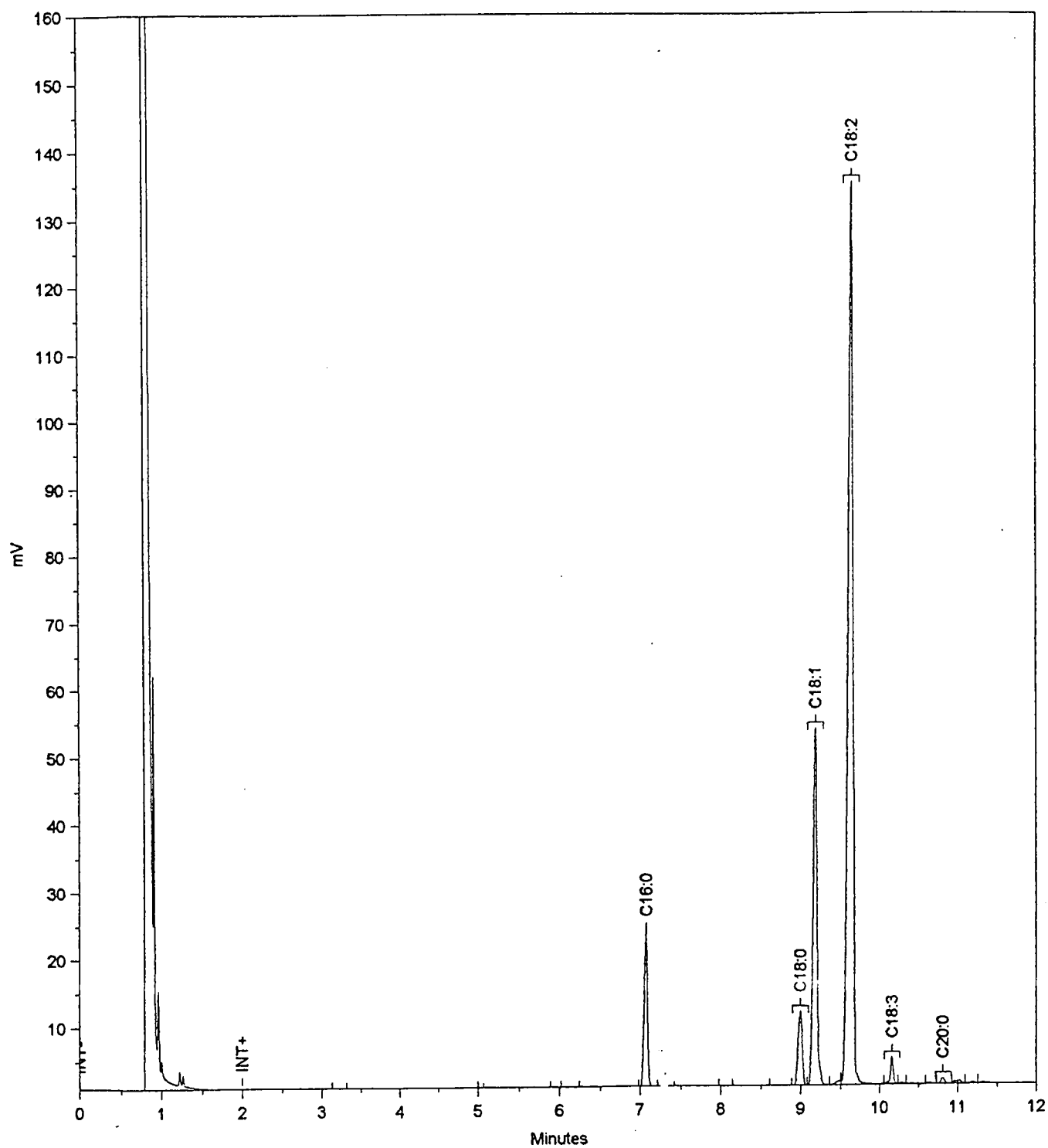


FIGURE 4.18  
CHROMATOGRAM OF FAME1.98R IN FRYING OIL SAMPLE 13 (AOCS)

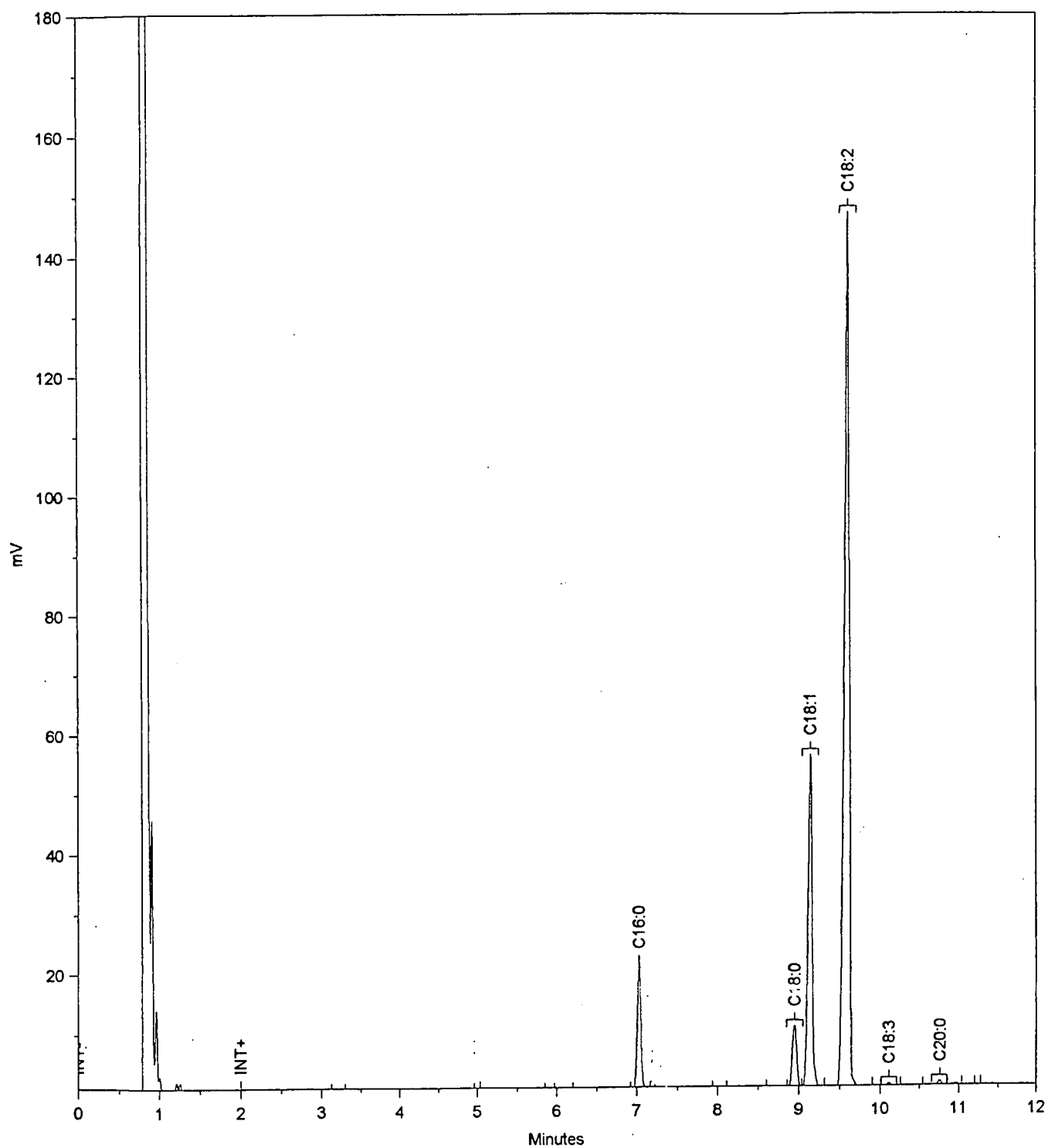


FIGURE 4.19  
CHROMATOGRAM OF FAME2.10R IN FRYING OIL SAMPLE 14 (AOCS)

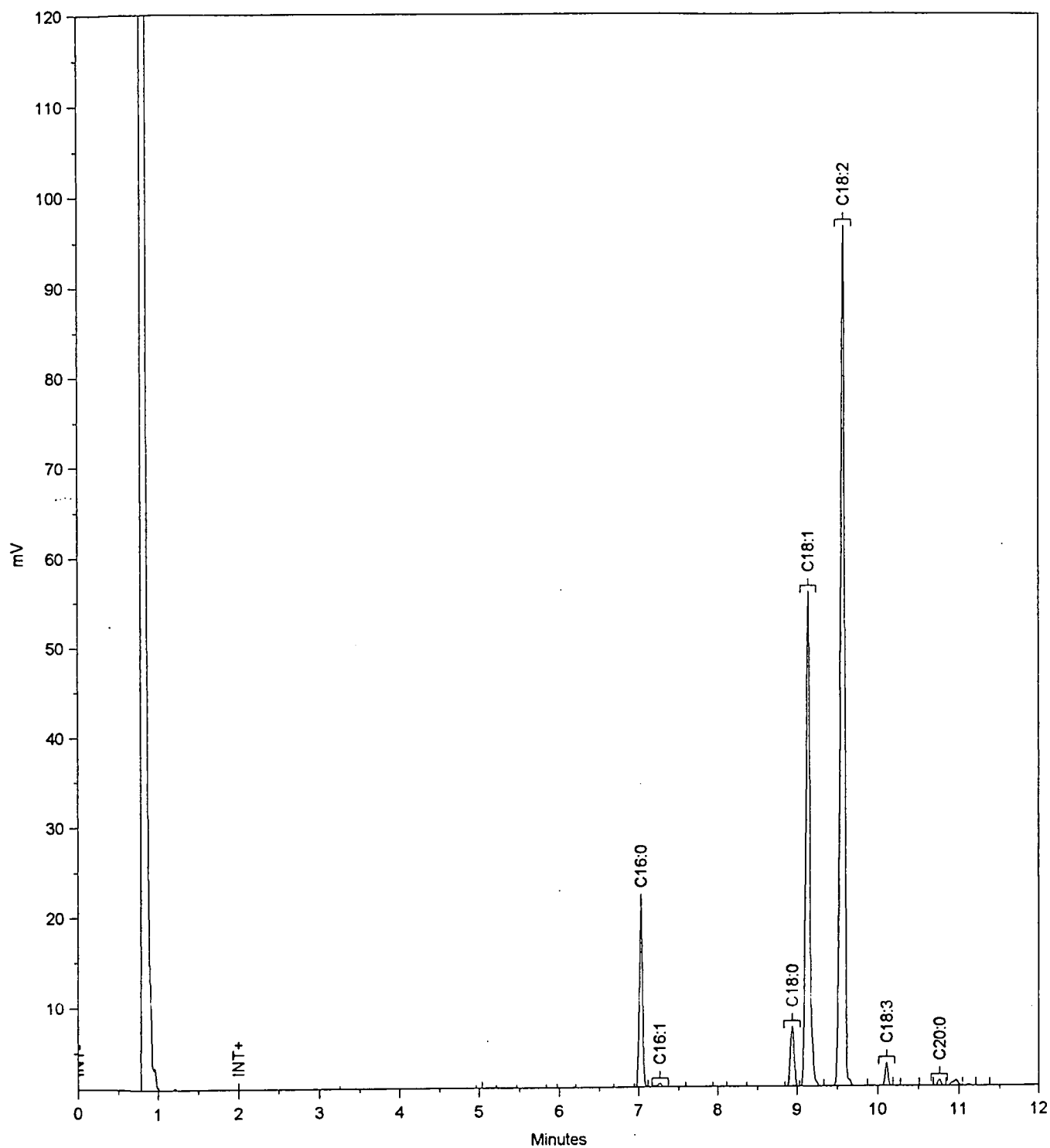


FIGURE 4.20  
CHROMATOGRAM OF FAME2.07R IN FRYING OIL SAMPLE 16 (AOCS)

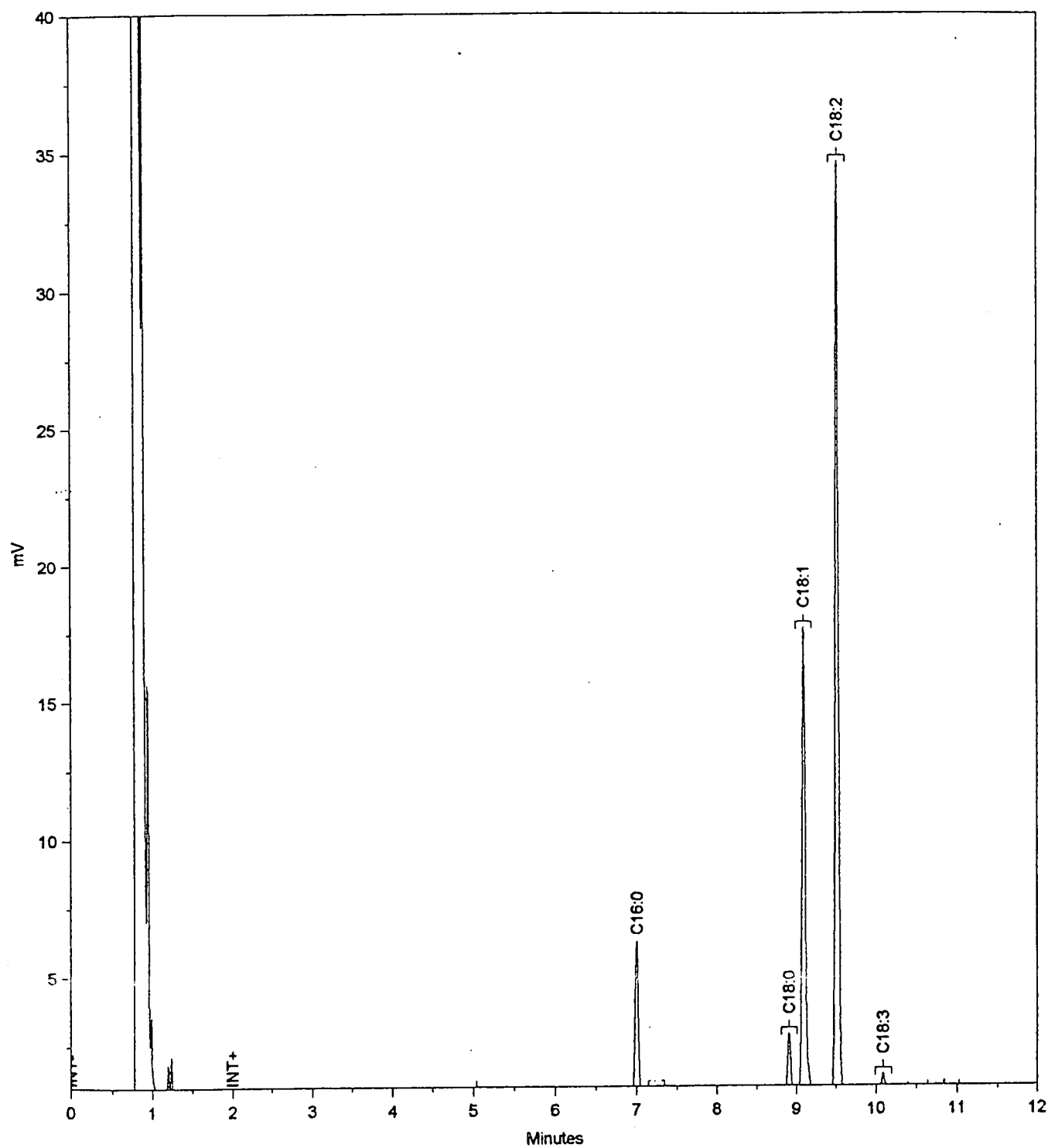


FIGURE 4.21  
CHROMATOGRAM OF FAME2.17R IN FRYING OIL SAMPLE 16 (ALT)

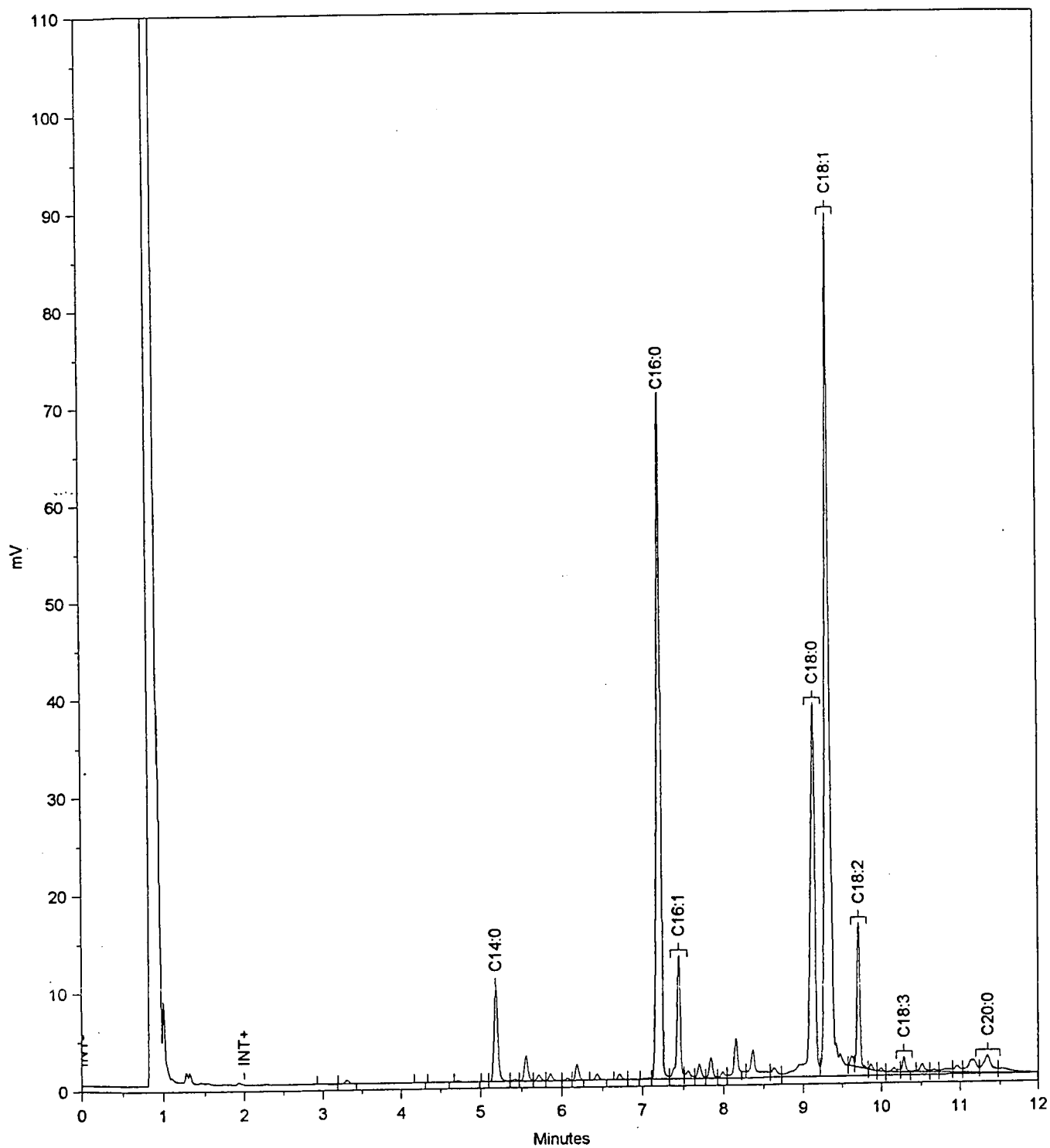


FIGURE 4.22  
CHROMATOGRAM OF FAME1.80R IN FRYING FAT SAMPLE 18 (AOCS)

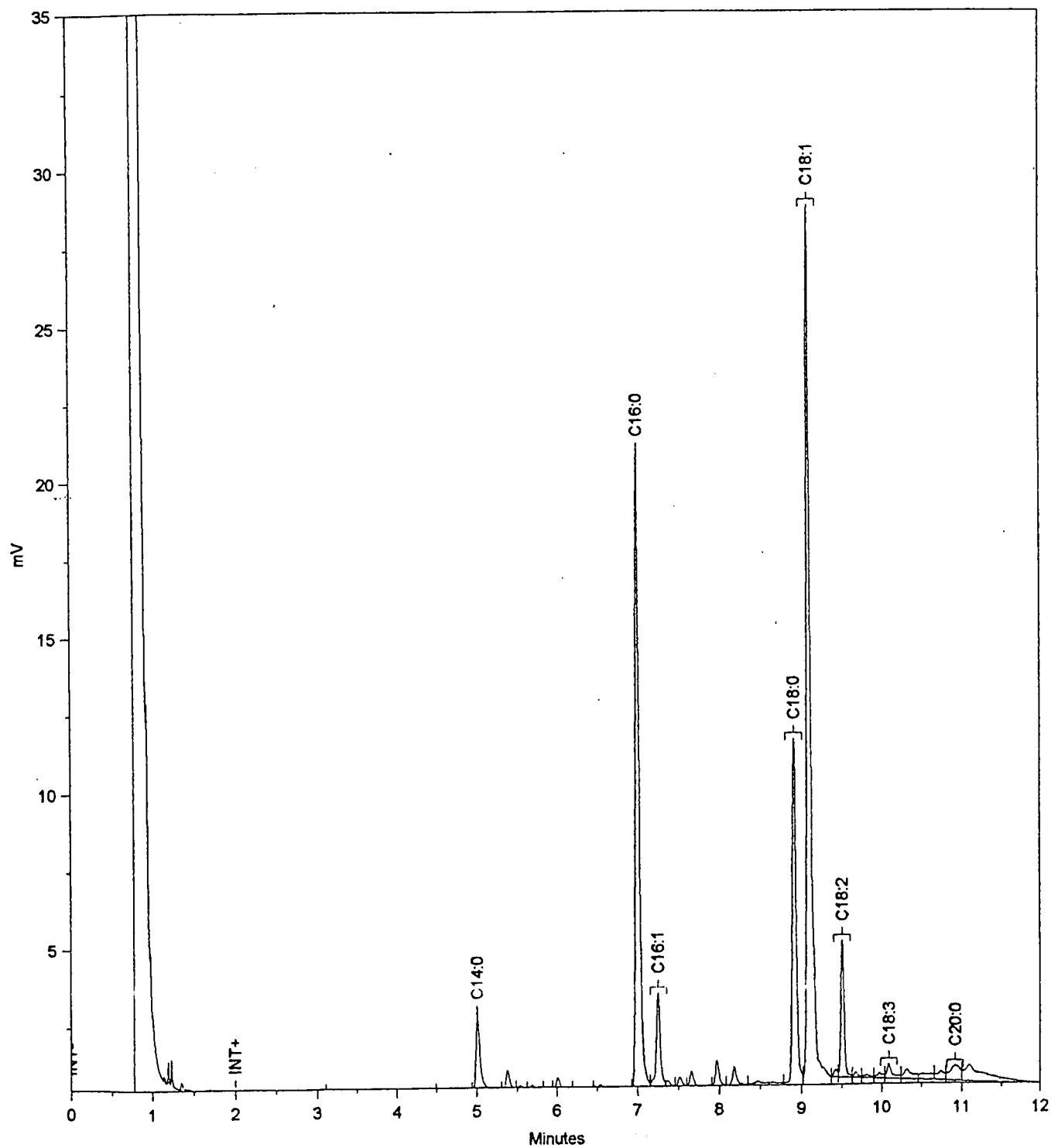


FIGURE 4.23  
CHROMATOGRAM OF FAME2.18R IN FRYING FAT SAMPLE 18 (ALT)



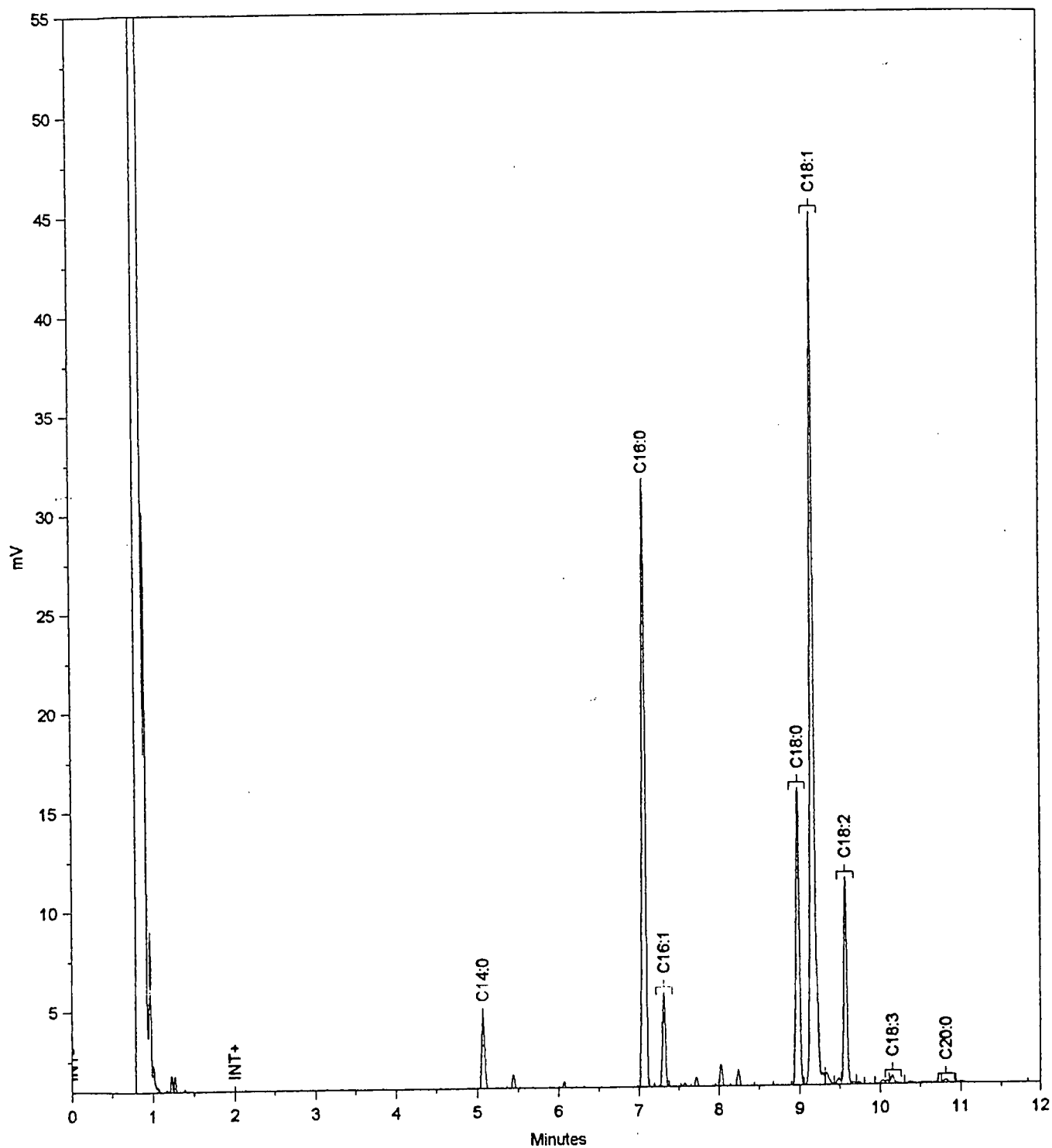


FIGURE 4.24  
CHROMATOGRAM OF FAME1.99R IN FRYING FAT SAMPLE 19 (AOCS)

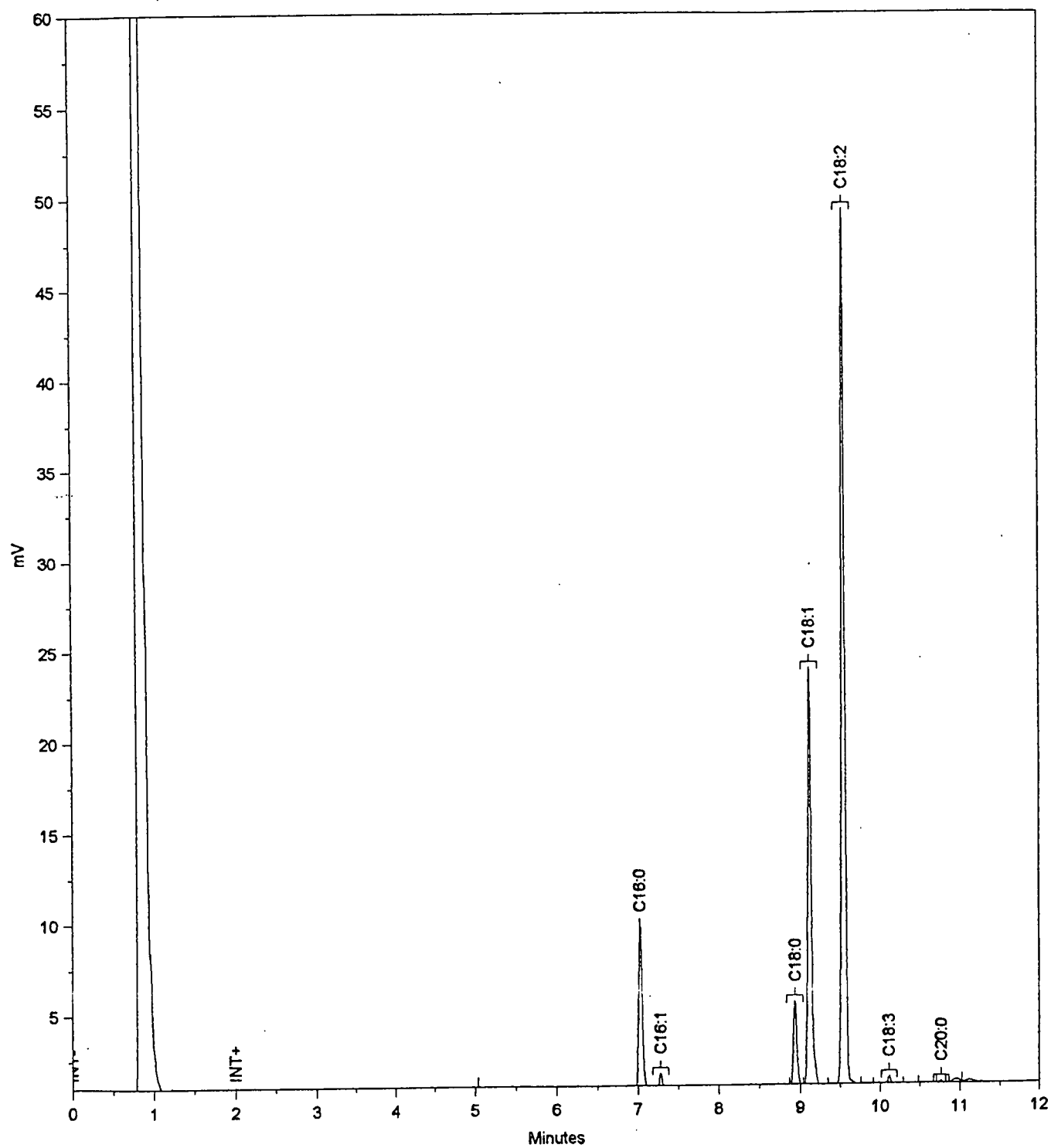


FIGURE 4.25  
CHROMATOGRAM OF FAME2.09R IN FRYING OIL SAMPLE 20 (AOCS)

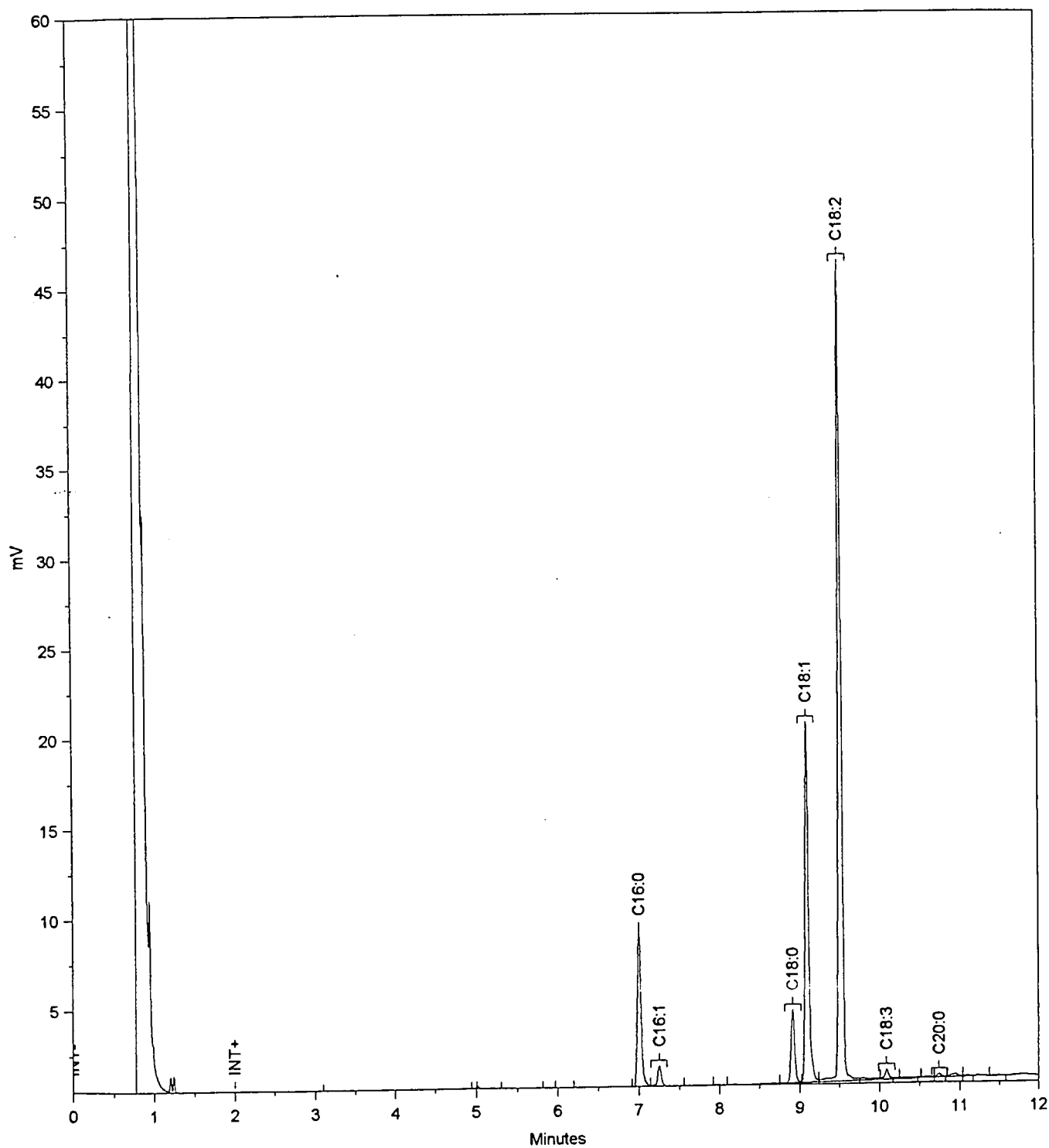


FIGURE 4.26  
CHROMATOGRAM OF FAME2.19R IN FRYING OIL SAMPLE 20 (ALT)

## CHAPTER 5

### 5.0 DISCUSSION OF RESULTS

#### 5.1 Determination of Free Fatty Acid and Acid Value Content

The results as shown in Table 4.1 confirmed to some extent that the Free Fatty Acid and Acid Value concentrations were affected by several factors. The increase in concentration was in proportion to the number of days that the frying fat or oil was in use. The increase was also caused by the types of food that were fried and by the presence of small food particles that remained in the frying medium during the frying process.

During the high frying temperatures, the water present in the food reacted with the frying medium which resulted in a hydrolysis reaction causing an increase in the concentration of Free Fatty Acids. The acceptable maximum concentration of Acid Value in used frying fats and oils that is recommended, internationally, is 2,5%. Frying oils having an Acid Value concentration of more than 3,0% leads to the oil becoming rancid, off-flavour and excessive smoking even at low frying temperatures

Eight of the samples analysed had an Acid Value concentration of less than 1,0%; seven of the samples analysed had an Acid Value that was close to the recommended maximum limit of 2,5% and five of the samples analysed had an Acid Value concentration of more than 2,5%. This showed that fifty-five percent

of the used frying oil samples analysed had deteriorated, were unacceptable for further use and should have been discarded. The analysis was also carried out on the unused helios and sunfoil oils and on the holsum fat to show the extent of use of the used frying oils and fats and for the purpose of comparison.

The Free Fatty Acid and Acid Value concentrations give some idea as to the condition of the frying fat or oil, but is a poor indicator for determining the fry-life.

## **5.2 Determination of Monoglycerides, Diglycerides and Triglycerides**

The analysis was determined on the unused helios oil and on seven, which ranged from the acceptable to the extremely unacceptable, of the twenty used frying oil samples obtained.

The analysis was carried out on each sample to observe the general trend, as the oil is used, in the increase in concentration of Monoglycerides and Diglycerides and the decrease in concentration of the natural Triglycerides and to compare the concentrations of these substances to that determined in the unused helios oil and the results are shown in Tables 4.2, 4.3 and 4.4 respectively.

The high concentration of the natural Triglycerides found in the fresh frying oils decreased gradually as the oil was used. This resulted, simultaneously, in an increase in concentration of Diglycerides, Monoglycerides, Oxidised Triglycerides and other substances. This was due to the various chemical reactions that occurred during the frying process.

The Monoglyceride, Diglyceride and Triglyceride fractions could be analysed further to determine the other substances present in them by utilising Gas Chromatography or High Pressure Liquid Chromatography. However, the analysis and the results obtained of these substances cannot be used to predict at what point the frying fat or oil should be discarded as there are many factors that affect the concentration of these substances.

### 5.3 Determination of Refractive Index

The Refractive Index was determined on all the used frying oil samples and compared with the Refractive Index of the unused helios and sunfoil oils and the holsum fat and the results are listed in Table 4.5. Majority of the values obtained were very close with the exception of a few which showed some differences.

This analysis is unsuitable to determine the life of the frying oil or fat as the Refractive Index is affected by the type of food fried and by the different food

colourings and food flavourings that are added during the frying process to improve the taste and the appearance of the fried foods.

#### **5.4 Determination of Peroxide Value**

The Peroxide Value indicates the degree of oxidation that has occurred in the frying fat or oil samples. The Peroxide Value was determined on all the used frying oil and fat samples obtained as well as on the unused helios and sunfoil oils and the holsum fat and the results are shown in Table 4.6.

The manufacturing process of the oil is very important in order to minimise the oxidation reaction. In fact, an oil that has been manufactured from good quality seeds and under controlled conditions should, initially, have a zero or a negligible Peroxide Value. The frying oils, even though in storage, can undergo oxidation reaction and the rate of oxidation depends on certain conditions, namely, the storage time, temperature and exposure to light and air. The Peroxide Value increases rapidly when the frying fat or oil is heated to the high frying temperatures.

Some of the values obtained, especially from those samples from the informal food preparation outlets, were very high in comparison with the values for the unused fat and oil samples indicating that the frying process was carried out

under unhygienic and terrible conditions. This was also evident with some of the samples obtained from the hotel, restaurant and franchise outlets.

The frying oils having a high Peroxide Value contain several decomposition products that are detrimental to health. Due to several factors that contribute to the oxidation of the frying oils, the Peroxide Value cannot be used to determine the life of the frying fat or oil.

### **5.5 The Polar and Non-polar content of Frying Fats and Oils**

The twenty used frying fat and oil samples and the unused helios and sunfoil oils and holsum fat were analysed to determine the concentrations of Polar and Non-polar Compounds and the results are listed in Tables 4.8 and 4.9 respectively.

The Polar Compounds include substances such as Monoglycerides, Diglycerides, and Free Fatty Acids which also occur, at low levels, in unused frying fats and oils. The concentration of these substances increase gradually during the frying of foods and during excessive heating of the frying medium. On the other hand, the Non-polar Compounds are predominantly unaltered or natural Triglycerides.

The Polar Compound concentration is used as an indicator to determine the condition of the frying fat or oil and the maximum acceptable limit allowed, by all



the Health Authorities in other countries which was a long time ago and recently accepted by Health Departments in South Africa, is 25%. Frying fats and oils having a concentration of more than 25% of Polar Compounds is regarded to be deteriorated and should be discarded.

A draft regulation to control the concentration of Polar Compounds present in frying fats and oils was published in the October 1995 Government Gazette by the Minister of Health and has been in operation since April 1996.

The results obtained from the used frying oils and fats show that six of the sample analysed had a Polar Compound concentration of more than 25%. Six of the samples had a Polar Compound concentration of between 20% and 25% and the remaining eight of the samples analysed had a Polar Compound concentration of less than 20%.

The five frying oil samples from the informal food preparation sector had a concentration of more than 25% of Polar Compounds. The samples from the franchise outlets and some samples from the hotels fell in the 20-25% Polar Compound concentration bracket.

This has indicated that about thirty-five percent of the samples had deteriorated at the time of sampling, were unfit for further use and should have been discarded.

### **5.6 Quality Assessment of Column Efficiency by T. L. C.**

The Chromatogram (Figure 4.1) illustrated the efficiency of the column after fractionating a used frying oil sample into Polar and Non-polar Compounds. This compared favourably with the chromatogram (Figure 4.2) obtained from the AOCS Official Method Cd 20-91.

This has shown that the T. L. C. Method is suitable to determine, both qualitatively and quantitatively, the Polar and Non-polar Compounds in frying fats and oils.

### **5.7 Determination of Viscosity of Frying Oils**

The Viscosity of all the used frying oil samples was determined and compared with that obtained for the unused helios and sunfoil oils. The values are listed in Table 4.10.

From the readings, it can be noted that the viscosity of the frying oil increased during the frying process. Frying sample 12 is holsum fat and was expected to remain in a solid state at room temperature even after being used for a long period of time. On the other hand, frying samples 17, 18 and 19 were, initially, liquid and on cooling to room temperature they turned solid. This indicated that these samples were extremely over used with the result that the fat from the fried food remained in the frying oil causing it to solidify at room temperature.

The types of food fried, especially meat, sausages, chicken and boerewors and the formation of degradation products that were produced during the frying process contributed to the increase in the viscosity of the frying oils. The increase in viscosity of the frying oils leads to an increase in the absorption of the frying oils into the fried food resulting in a poor quality of fried food being produced.

The viscosity reading of frying oils cannot be used to determine at what point should the frying oils be discarded due to several factors that contributes to its effect.

## **5.8 Qualitative Analysis of Fatty Acid Methyl Esters (FAME) in Frying Fats and Oils**

A few randomly selected frying oil and fat samples were used, at first, for the preparation of FAME by two different methods and, thereafter, for these FAME samples to be analysed by the Capillary Gas Chromatographic method to identify, qualitatively, the different Fatty Acid Methyl Esters that were present in the frying fats and oils. The Chromatograms obtained from the analysis of these FAME samples are illustrated from Figure 4.3 to Figure 4.26.

The chromatograms of the standard Fatty Acid Methyl Ester samples (Figure 4.3) showed the presence of Palmitic(C16:0), Stearic(C18:0), Oleic(C18:1),

Linoleic(C18:2), Linolenic(C18:3) and Arachidic(C20:0) acid methyl esters and (Figure 4.4) showed the components Myristic(C14:0), Palmitic(C16:0), Palmitoleic(C16:1), Stearic(C18:0) and Oleic(C18:1) acid methyl esters.

The chromatogram of the unused helios oil showed the presence of Palmitic, Stearic, Oleic and Linoleic acid methyl esters in abundance and traces of Linolenic and Arachidic acid methyl esters (Figure 4.5). The most common Fatty Acid Methyl Esters present in abundance in all the used frying fat and oil samples as shown on the respective chromatograms were Palmitic, Stearic, Oleic and Linoleic acid methyl esters.

Some of the frying oil samples had traces of Palmitoleic, Linolenic and Arachidic acid methyl esters. In addition to the common Fatty Acid Methyl Esters, there were large amounts of Myristic, Palmitoleic, Linolenic and Arachidic acid methyl esters and other substances present in frying fat and oil samples 18 and 19 (Figure 4.22, Figure 4.23 and Figure 4.24). These frying oil samples were from the informal food preparation outlets and the results shows that these samples were extremely abused.

From the chromatograms obtained it can be concluded that there was no difference in the two methods used to prepare the Fatty Acid Methyl Esters.

## 5.9 PERSONAL INTERVIEWS AND OBSERVATIONS

A random survey was conducted at twenty formal food preparation outlets and a few of the informal food traders in the Durban Central and surrounding townships and those persons responsible at these food preparation establishments were interviewed on the following:-

- (a) The method used to determine at what point is the frying oil unfit for further use.

<u>No. of Outlets</u>	<u>Response from Formal Outlets</u>
14	Depended on the colour, taste and appearance of the fried foods and the visual colour of the frying oil.
6	Depended on the Standard Lovibond colour monitor. These were some of the very large restaurants and franchise businesses.

(b) The method of disposal of the used frying oils.

<u>No. of Outlets</u>	<u>Response from Formal Outlets</u>
11	Sold the used frying oils to their staff or to the informal fried food outlets.
3	Did not discard the used frying oils, but instead, filtered off the tiny food particles from the used frying oil and added fresh oil when it was necessary.
3	Collected the used frying oils into large (25 litre) plastic containers and sold to "entrepreneurs" who then re-sold the used oils in smaller quantities to the domestic households in the townships and rural areas.
2	Sold some of the used oil to the staff members and re-used the remainder to prepare their mutton, chicken and fish curries.
1	Dumped the used frying oil in their privately owned disposal site.

All of the informal fried food traders that were interviewed conducted their businesses at major shopping centres in the surrounding townships in open areas close to the taxi and bus terminals and also at strategic locations where there was a large number of people doing their shopping. The response from the responsible people in the informal food preparation outlets was very poor, disappointing and some of them even behaved aggressively.

<u>No. of Outlets</u>	<u>Response from Informal Outlets</u>
5	Refused to give any information on the disposal of the used frying oils and also at what stage should the frying oil be discarded.
3	Obtained the used frying oils from the formal outlets and did not discard the re-used oil.
2	Did not discard the used frying oil. Added fresh oil when required.

Majority of these informal traders either could not find employment or were retrenched from their previous employments due to reduction of staff or the closure of the businesses. Some of these informal traders conducted their food

frying businesses only on week-ends when the centres were bustling with shoppers in order to subvent their meagre salaries. These people found that the preparation and sale of fried foods to be a lucrative and profitable business with no or very little cost incurred.

Majority of the formal fried food establishments used the large deep-frying type of electric friers equipped with a thermostat to maintain the frying fat or oil at the optimum frying temperature and a suitable drainage system to drain off the excess fat or oil from the fried foods (Figures 6.1, 6.2 and 6.3).

The most common type of friers used by the informal traders were the portable skottel or the rectangular solid plate with a handi-gas cylinder to supply the heat (Figures 6.4, 6.5 and 6.6). By using such type of frying apparatus the oil was absorbed into the food. The quality of the oil deteriorated further due to the prolonged overheating of the oil.

Some of the formal and majority of the informal traders claimed that they had no knowledge that ill-health and certain diseases were associated with the usage of old used frying oils. The major concern was that majority of the personnel from both the formal and informal food preparation outlets, even after being advised of the harmful effects on the use of abused frying oils, were not at all interested or prepared to deviate from their bad cooking habits.



The traders said that if they followed the strict regulations, they would have to purchase and use more fresh cooking oil thus increasing their cost which they believe will, eventually, be passed onto the consumers by increasing the selling price. This will affect the sales of fried foods and the profit margin considering that a large percentage of the consumers that patronised, especially the informal food frying outlets, came from the lower income group. The fried foods prepared and sold by these informal outlets were much cheaper and of poorer quality than those fried foods prepared and sold by the formal outlets.

I did not interview the informal traders who conducted their businesses in the City, more especially the Warwick Avenue Complex, for fear of being threatened as they felt that I may report them to the Health Authorities who will close down their business.

However, I did observe the storage, handling and the frying process of the foods. The uncooked foods, especially the meat, sausages and boerewors which were stored in large styrofoam cooler boxes, were dipped into a bucket of water and washed and then placed onto the pre-heated skottel or rectangular solid plate which contained some dark coloured used frying oil. The fried foods were then placed onto styrofoam trays and displayed on tables made from wooden pallets under extremely un-hygienic conditions on the pavements along-side the road.

These fried foods were exposed to the dust from the road-side and atmosphere and to the exhaust fumes from all the motor vehicles and not to mention the flies.

There was a plastic container of oil kept aside and this oil was added to the frier whenever it was required to prepare more fried foods. From the dark colour of the oil and the rancid smell emanating from the frier, one could be very certain that the oil added to the frier was previously abused.

The above interviews and observations indicated the extreme insensibility of the unscrupulous food preparation traders and it seems that this City is sitting on a time bomb ready to erupt with disastrous health consequences.

## CHAPTER 6

### 6.0 CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 CONCLUSIONS

Fried foods, such as potato chips, meat, chicken, sausages, fish and boerewors form a major part of the diet of majority of the South African population. It is essential that these fried foods are of good quality. This can only be achieved with the use of good quality frying fats and oils and the frying process carried out under strict control and hygienic conditions.

It must be pointed out that the frying fat and oil samples were collected by the Environment Health Officer without prior notification to the formal and informal food preparation establishments. Some of the frying oil samples obtained were in good condition. However, this did not necessarily mean that the management from these food frying establishments adhered to the strict control with regards to the replacement of the used frying fats and oils and to monitoring the frying process.

The various analyses have indicated that the general quality of the frying fat and oil samples were extremely poor. This was evident especially when these

samples were analysed to determine the concentrations of Acid Value, Peroxide Value and Polar Compounds. All the frying oil samples from the informal sector and some of the samples from the hotel, restaurant and franchise sectors were extremely abused. Forty percent of the frying oil samples collected were used for more than four days and this repeated and intermittent heating, frying and cooling processes and the storage and handling of these samples contributed to the deterioration and poor quality of the frying oils.

The Durban Metro Health Department, initially, did not analyse the frying fats and oils for their degradation products. However, they performed tests on the prepared foods for any microbial or bacterial contamination.

Since the publication of the draft regulation in April 1996 by the Directorate: Food and Chemicals of the Department of Health, more attention has now been directed to monitoring the quality of frying fats and oils. They have, at present, about two thousand of these fried food establishments under their control and are finding it extremely difficult to keep control and monitor their bad cooking habits as the numbers, especially the informal traders, are increasing daily.

The general attitude of majority of the suppliers of fried foods is to sell their fried food products with the least cost incurred by whatever means and to have a complete disregard for the well-being and health of the consumers.

Presently, there are three rapid "on the spot" tests, namely, the Oxifrit Test, the Fritest and the Veri-Fry Colorimeter Test, that are available for the testing of frying fats and oils. The Oxifrit Test and the Fritest can only be used to analyse frying fats and oils at room temperature, whereas, the Veri-Fry Colorimeter Test can be used to determine the degree of deterioration on the hot frying fat or oil. This is of great advantage as far as the saving on time is concerned.

## 6.2 RECOMMENDATIONS

The findings of this research project is extremely shocking and of great concern, especially to the Health Authorities and the people who purchase and consume fried foods on a daily basis. There is an urgent need for strict legislation to be implemented to control and monitor, on a regular basis, the conditions under which foods are fried, the use or sale of abused frying fats and oils and the disposal of the used frying oils.

The Health Authorities should recommend or make it compulsory for all the establishments in the fried food industry to make use of any one of the three rapid test kits available in order to monitor the quality of their frying fats and oils.

There is also a need for the personnel from both the formal and informal food frying establishments and the general consumers to be educated on the harmful

effects of preparing and consuming foods that are fried or cooked in abused frying fats and oils.

### **6.2.1 Hints and Tips on the Use of Frying Oils**

One of the biggest expenses in the fried food industry is the oil used for frying or cooking. By following the simple guidelines, the cost effectiveness of oil usage can be greatly improved which will result in good quality of fried foods, more satisfied customers leading to bigger turnovers and better profits.

- (a) Buy the best quality cooking oil available.
- (b) Heat the oil slowly.
- (c) Maintain a constant temperature of the oil during the frying process. Do not heat the oil over 180° C.
- (d) Avoid the use of a copper or bronze based frier that is in contact with the heated frying oil.
- (e) Achieve an oil replacement rate of over 30%.
- (f) Filter the oil daily and remove loose particles from the surface regularly.
- (g) Clean the frier daily.
- (h) Keep the frying oil covered when not in use.
- (l) Use only good oil in pressure frying.

- (j) Maintain an oil to food ratio of no more than 6 to 1 for each frying batch.  
Overloading of a frier causes a decrease in frying temperature which results in longer frying time, slower food production and greasier foods.
- (k) Do not use oil that is deteriorating.
- (l) Make sure that the food portions are all of the same size.
- (m) Reduce the residue of batter or bread-crumbs and use batter wherever possible.
- (n) Allow frozen foods to thaw before frying.
- (o) Remove all excess moisture from foods.
- (p) Soak potato chips in water to remove all excess starch and then drain well before frying.



FIGURE 6.1

FRYING EQUIPMENT USED IN FORMAL SECTOR



FIGURE 6.2

EXCESS FRYING OIL DRAINED FROM FRIED POTATO CHIPS





FIGURE 6.3

FOAMING OF FRYING OIL DURING THE FRYING OF POTATO CHIPS



FIGURE 6.4

FRYING EQUIPMENT (SOLID PLATE) USED IN THE INFORMAL SECTOR



FIGURE 6.5

FRYING EQUIPMENT (SOLID PLATE) USED IN THE INFORMAL SECTOR





FIGURE 6.6

FRYING EQUIPMENT (SKOTTEL) USED IN THE INFORMAL SECTOR

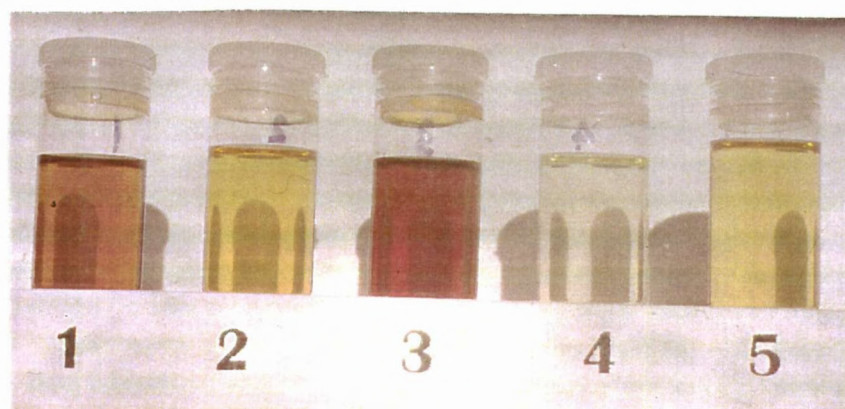


FIGURE 6.7

FRYING OIL SAMPLES FROM THE HOTELS

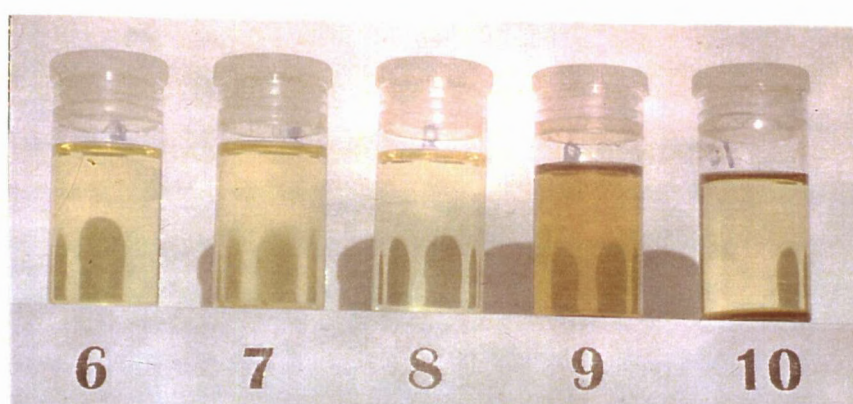


FIGURE 6.8

FRYING OIL SAMPLES FROM THE RESTAURANTS AND TAKE-AWAYS



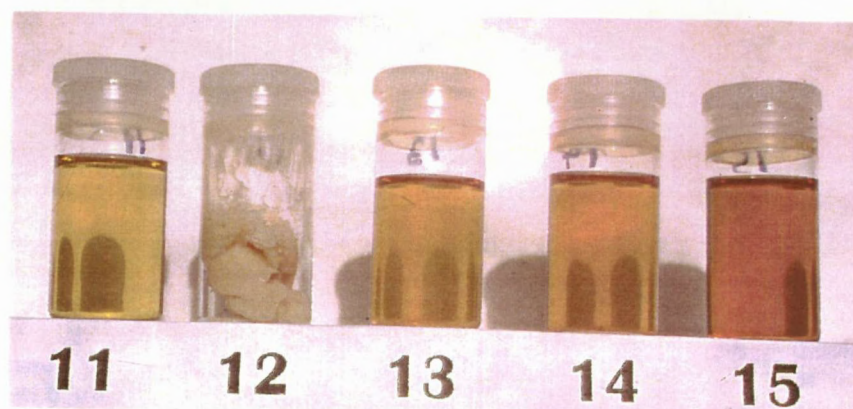


FIGURE 6.9

FRYING OIL SAMPLES FROM THE FRANCHISE OUTLETS



FIGURE 6.10

FRYING OIL SAMPLES FROM THE INFORMAL OUTLETS

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## APPENDICES

### APPENDIX A

#### PREPARATION AND STANDARDISATION OF SODIUM HYDROXIDE SOLUTION FOR THE DETERMINATION OF FREE FATTY ACIDS

##### PREPARATION OF SODIUM HYDROXIDE (NaOH) SOLUTION

Approximately 4g of Sodium Hydroxide pellets was massed, using a top-loading balance, into a one litre volumetric flask. Distilled water was added, at first, to dissolve the pellets and, thereafter, more distilled water was added to the mark and the flask shaken.

##### PREPARATION OF STANDARD POTASSIUM HYDROGEN PHTHALATE (KHP) SOLUTION

Approximate mass of KHP required to prepare 0,25 dm<sup>3</sup> of approximately 0,1 mol dm<sup>-3</sup> solution =  $0,1 \text{ mol dm}^{-3} \times 204,22 \text{ g mol}^{-1} \times 0,25 \text{ dm}^3 = \underline{5,1\text{g}}$

The KHP was massed, using a top-loading balance, into a clean, dry polytop and then re-massed on the analytical balance. The KHP was transferred quantitatively into a clean 250 cm<sup>3</sup> volumetric flask and the empty polytop was

## APPENDIX A (cont.)

re-massed. Distilled water was added to dissolve the KHP and then topped-up to the mark with more distilled water and the flask was shaken.

$$\begin{aligned}\text{Mass of polytop + KHP} &= 9,4275\text{g} \\ \text{Mass of polytop} &= \underline{4,3088\text{g}} \\ \text{Mass of KHP} &= \underline{5,1187\text{g}}\end{aligned}$$

$$\begin{aligned}\text{Molarity of KHP Solution} &= \frac{5,1187\text{g}}{204,22\text{g mol}^{-1}} \times \frac{1}{0,25\text{ dm}^3} \\ &= \underline{0,10025\text{ mol dm}^{-3}}\end{aligned}$$

### STANDARDIZATION OF NaOH SOLUTION

Flask contained : 20,00 cm<sup>3</sup> of 0,10025 mol dm<sup>-3</sup> KHP Solution.

Burette contained : Approx. 0,1 mol dm<sup>-3</sup> NaOH Solution.

Indicator used : 3 drops Phenolphthalein

Colour change : colourless → pink

	1.	2.	3.
Final burette reading (cm <sup>3</sup> )	18,30	36,60	18,30
Initial burette reading (cm <sup>3</sup> )	<u>00,00</u>	<u>18,30</u>	<u>00,00</u>
Volume delivered (cm <sup>3</sup> )	<u>18,30</u>	<u>18,30</u>	<u>18,30</u>

$$\text{Mean volume delivered} = \underline{18,30\text{ cm}^3}$$



## APPENDIX A (cont.)

Calculation :

$$\text{No. of moles of KHP} = 0,10025 \text{ mol dm}^{-3} \times 20,00 \times 10^{-3} \text{ dm}^3$$

$$= 2,005 \times 10^{-3} \text{ moles}$$

$$\text{No. of moles of NaOH} = 2,005 \times 10^{-3} \text{ moles}$$

$$\text{Mean volume of NaOH} = 18,30 \times 10^{-3} \text{ dm}^3$$

$$\text{Molarity of NaOH} = \frac{2,005 \times 10^{-3} \text{ moles}}{18,30 \times 10^{-3} \text{ dm}^3}$$

$$= \underline{0,1096 \text{ mol dm}^{-3}}$$

## APPENDIX B

### PREPARATION AND STANDARDISATION OF SODIUM THIOSULPHATE SOLUTION FOR THE DETERMINATION OF PEROXIDE VALUE

#### PREPARATION OF APPROXIMATELY $0,01 \text{ mol dm}^{-3}$ SODIUM THIOSULPHATE ( $\text{Na}_2\text{S}_2\text{O}_3$ ) SOLUTION

Massed out about 2,5g of Sodium Thiosulphate, using a top-loading balance, and dissolved it with freshly boiled out distilled water in a one litre volumetric flask to the mark.

#### PREPARATION OF STANDARD POTASSIUM IODATE ( $\text{KIO}_3$ ) SOLUTION

$$\begin{aligned}
 \text{Mass of Polytop + Potassium Iodate} &= 5,1302\text{g} \\
 \text{Mass of Polytop} &= \underline{5,0027\text{g}} \\
 \text{Mass of Potassium Iodate} &= \underline{0,1275\text{g}} \\
 \\ 
 \text{Molarity of Potassium Iodate} &= \frac{0,1275\text{g}}{214,00\text{g mol}^{-1}} \times \frac{1}{0,25 \text{ dm}^3} \\
 &= \underline{2,3832 \times 10^{-3} \text{ mol dm}^{-3}}
 \end{aligned}$$

## APPENDIX B (cont.)

## STANDARDIZATION OF SODIUM THIOSULPHATE SOLUTION

Flask contained : 20,00 cm<sup>3</sup> of 2,3832 x 10<sup>-3</sup> mol dm<sup>-3</sup> KIO<sub>3</sub> Solution  
2g Potassium Iodide and 5 cm<sup>3</sup> of 1M H<sub>2</sub>SO<sub>4</sub> Solution

Burette contained : Approx. 0,01M Sodium Thiosulphate Solution

Indicator used : 2 cm<sup>3</sup> of 1% Starch Solution

Colour changes : dark orange → pale yellow ; blue → colourless

	1.	2.	3.
Final burette reading (cm <sup>3</sup> )	28,50	28,40	28,45
Initial burette reading (cm <sup>3</sup> )	<u>00,00</u>	<u>00,00</u>	<u>00,00</u>
Volume delivered (cm <sup>3</sup> )	<u>28,50</u>	<u>28,40</u>	<u>28,45</u>

Mean volume delivered = 28,45 cm<sup>3</sup>

Reaction equation :  $\text{IO}_3^- + 8\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_3^- + 3\text{H}_2\text{O}$

$\text{I}_3^- + 2\text{S}_2\text{O}_3^{2-} \rightarrow 3\text{I}^- + \text{S}_4\text{O}_6^{2-}$

$3\text{I}_3^- + 6\text{S}_2\text{O}_3^{2-} \rightarrow 9\text{I}^- + 3\text{S}_4\text{O}_6^{2-}$

Reaction ratio : 1 KIO<sub>3</sub> : 6 Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

Calculation

No. of moles of KIO<sub>3</sub> = 2,3832 x 10<sup>-3</sup> mol dm<sup>-3</sup> x 20,00 x 10<sup>-3</sup> dm<sup>3</sup>

= 4,7664 x 10<sup>-5</sup> moles

No. of moles of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 4,7664 x 10<sup>-5</sup> moles x 6

= 2,8598 x 10<sup>-4</sup> moles

## APPENDIX B (cont.)

$$\text{Mean volume of Na}_2\text{S}_2\text{O}_3 = 28,45 \times 10^{-3} \text{ dm}^3$$

$$\begin{aligned} \text{Molarity of Na}_2\text{S}_2\text{O}_3 \text{ Solution} &= \frac{2,8598 \times 10^{-4} \text{ moles}}{28,45 \times 10^{-3} \text{ dm}^3} \\ &= \underline{0,01005 \text{ mol dm}^{-3}} \end{aligned}$$

## FORMULA FOR THE CALCULATION OF PEROXIDE VALUE

Peroxide Value ( millimoles of peroxide per 1000g of sample )

$$= \frac{(S - B) \times M \times 1000g}{\text{Mass of Sample (g)}}$$

where :

S = Titration volume of Sample ( $\text{cm}^3$ )

B = Titration volume of Blank ( $\text{cm}^3$ )

M = Molarity of Sodium Thiosulphate Solution ( $\text{mmol cm}^{-3}$ )



## APPENDIX C

### PREPARATION OF METHYL ESTERS OF LONG-CHAIN FATTY ACIDS

#### (AOCS-METHOD)

The sample was massed into a 50cm<sup>3</sup> round bottom flask. 6cm<sup>3</sup> of 0,5M NaOH in Methanol Solution was added and the solution was refluxed for 5-10 minutes. 7cm<sup>3</sup> of BF<sub>3</sub> - Methanol mixture was added and then boiled for 2 minutes. About 3cm<sup>3</sup> of Hexane was added and the solution boiled for a further 1 minute. The solution was cooled and about 15cm<sup>3</sup> of Saturated Sodium Chloride Solution was added, the flask stoppered and shaken vigorously for about 15 seconds.

More saturated sodium chloride solution was added until the hexane layer came up to the neck of the flask. The hexane layer was transferred, using a pasteur pipette, into a sample tube containing about 1g of anhydrous sodium sulphate as a drying agent. The dry hexane layer was injected into the Gas Chromatograph capillary column for the analysis of fatty acid methyl esters present in the frying fats and oils and, thereafter, stored in the refridgerator to prevent any decomposition.

## APPENDIX D

### PREPARATION OF FATTY ACID METHYL ESTERS

#### ALTERNATE (ALT) METHOD

In this method, Concentrated Sulphuric Acid, an acid, was used compared to the use of Methanolic Sodium Hydroxide, a base, in the AOCS Official Method. The sample was massed directly into a 50cm<sup>3</sup> round bottom flask. About 20cm<sup>3</sup> of pure Methanol and 2 drops of concentrated Sulphuric Acid was added.

The solution was refluxed for 1 hour. 5cm<sup>3</sup> of hexane was added via the condensor and the refluxing continued for 2 minutes. The solution was cooled and about 15cm<sup>3</sup> of saturated Sodium Chloride solution was added, the flask stoppered and shaken vigorously for 15 seconds.

More saturated sodium chloride solution was added until the hexane layer came up to the neck of the flask. The hexane layer was pipetted into a sample tube which contained anhydrous sodium sulphate as a drying agent. The sample was injected into the Gas Chromatograph capillary column for the analysis of FAME and, thereafter, stored in the refrigerator to prevent any deterioration.