THE EVALUATION AND SIGNIFICANCE OF DETERIORATION IN FRYING FATS

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Lois Elaine Jeffery

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ABSTRACT

Jeffery, Lois Elaine. M. Sc. The University of Manitoba, October, 1982. The Evaluation and Significance of Deterioration in Frying Fats. Major Professor; Dr. F.W. Hougen.

Canola frying fats and newer methods for determination of frying fat quality were evaluated in a simulated commercial frying study using french fried potatoes. Two brands of canola frying fat and one brand of soy frying fat were used consecutively to fry frozen french fries in a small institutional size deep fryer for a total of five 8-hour days. Samples of the frying fat and the french fries were collected throughout the frying period and were used for a number of physical and chemical analyses. Free fatty acid (FFA) values were determined for samples of frying fats and for samples of fats extracted from the french fries. The FFA values appeared to be very sensitive to the changes taking place in the deep fryer, and were similar for both the frying fats and fats extracted from the french fries. The FFA values for the soy frying fat were slightly higher than the values for either of the two canola fats throughout the 5 days of frying. Three different methods for estimation of total polar components were evaluated. Change in dielectric constant as measured by the Foodoil Sensor did not appear to be a reliable or sensitive measurement. A reported liquid column chromatographic method, when reduced to one-quarter scale, offered considerable savings in time and materials and proved as sensitive and reproducible as the full scale method. Another chromatographic technique, using thin-layer chromatography on chromarods with quantitation by a flame ionization detector (the Iatroscan Analyzer) was not as accurate or reproducible as the column chromatographic method, but offered a rapid method for monitoring deterioration in frying fats. Standardization of the technique is very important and could still be improved. Results are qualitative as well as quantitative and the system is reusable. Results of column chromatographic separation of the three frying fats over the five days of frying indicated that only a moderate amount of deterioration, producing 12-13% polar components, had taken place. There was very little difference in the degree of deterioration among the three brands of fats.

INTRODUCTION

The evaluation of frying fats is of concern to several groups. Nutritionists have long been interested in the types of degradation products in heated fats and their effects on human nutrition. The food industry is interested in, as well, how degradation products affect the quality of the fried products and the frying life of the fat. It is also important for the processors to have information on different types of fats and oils, particularly canola oil which in Canada now accounts for more than one-third of our edible oil (Statistics Canada, 1981) and of which there is little published information available. Thus, it is important to have quick, meaningful tests of the quality of frying fats.

It appears from a review of the literature that the methods for estimation of total polar components in heated fats are the most useful for determining the quality of fats under varying conditions of use. However, most of these methods are time-consuming or expensive and the challenge remains to develop a quicker method which would be applicable for routine quality control. Thus, one aim of this research was to evaluate some of the methods for determination of polar components.

A second aim of the study was to obtain additional information on the behavior of canola frying fats under conditions of simulated commercial deep frying.

This study was carried out as a joint project between the Departments of Foods and Nutrition,and Plant Science. The actual deep fat frying was carried out in the Department of Food Science. Some of the analytical work was carried out in the Department of Foods and Nutrition and is presented, along with the statistical analysis of the results, in the manuscript appendixed to this thesis. The analytical work carried out in Plant Science by the author is described in detail with the results in the thesis, while some results are also included in the manuscript.

The following review of the literature will present some of the reasons for the interest in evaluation of frying fat quality and a discussion of the methods used in this study.

REVIEW OF LITERATURE

I. The Role of Frying Fat in Foods

Deep frying is a popular and widely accepted method of cooking numerous food items. Foods prepared by this method are well liked because of characteristics conferred by the frying process. The raw food is immersed in hot fat where it is quickly cooked so that the interior remains moist while a uniform crispy brown crust forms over the outside, giving the cooked product an appealing appearance and flavour (Robertson, 1967).

Deep frying is a widely used method of cooking in the food industry because it is fast, uniform and produces products with high consumer appeal. With a steady increase in consumption of snack foods and meals eaten away from home, deep fried foods may form a substantial portion of the diet. As fried foods contain from 7-40% frying fat (Jacobson, 1967), the frying fat itself becomes an integral part of the diet.

It is well established that frying fat held for long periods of time at temperatures of 175-200^{o}C, in the presence of oxygen and water, partially decomposes forming numerous volatile and non-volatile compounds. Artman (1969) has reviewed the chemical changes which take place and the various classes of degradation products formed. Chang et al (1978) has identified more than 200 individual chemical compounds in the volatile fraction of the frying fat alone. Fritsch (1981) has provided a very general diagramatic outline of

the varous reactions which take place in the frying kettle (Fig. 1). At some point in the frying life of the fat these degradation products reach a level at which they begin to adversely affect the quality of the fried products, and finally the user must discard the fat. It is the composition of the frying fat up to this point and its subsequent effect on human nutrition which have most concerned researchers in this area for the past three decades. More recently, there has been an increase in the research on heated frying fats from the point of view of the food industry. In a market in which prices and types of fats available are rapidly changing, the food processors are interested in the deterioration of fats in terms of product quality. The processor must produce a product which consumers like and which has good shelf life. Thus, they must monitor degradation products which affect the palatability and stability of the finished products. Both groups are interested in having quick tests to evaluate the quality of the frying fat during use, and in knowing at which point in the frying life of the fat either product quality or nutritive value may be affected.

However, despite the many sophisticated analytical methods available for analysis of fats and oils, there are few which prove of much use to the food industry. Often they are too time-consuming or too complicated, or their relationship to the sensory qualities of the food products are not clear. In practice, in small commercial operations and especially in the home, the frying fat is discarded on the basis of some undefined methods of sensory evaluation by the user. Large commercial operations, especially those

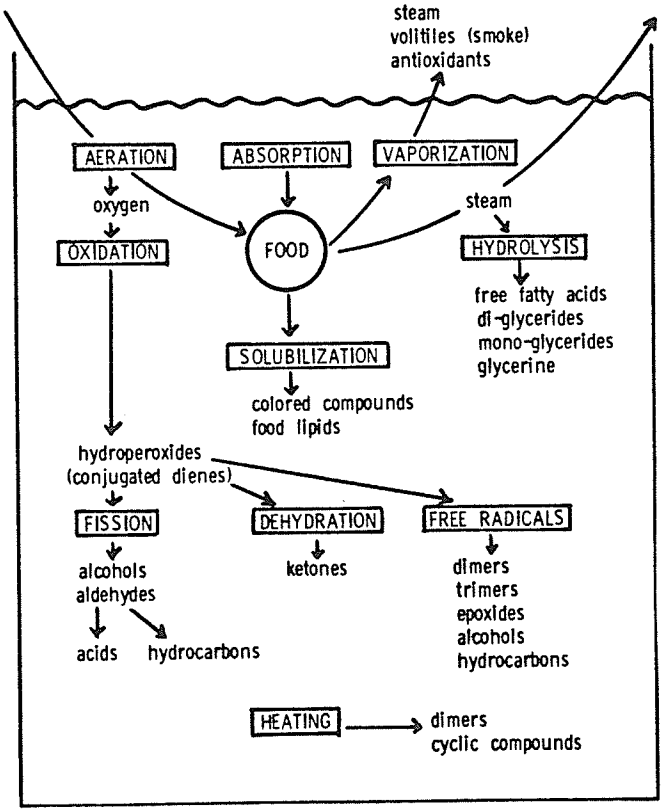

Figure 1: Changes occurring during deep fat frying (from Fritsch, 1981).

involved in frying snack food items which must have good shelf stability, monitor the quality of frying fats closely and discard the fat immediately if it appears to be affecting product quality. Since products such as snack foods absorb a large amount of fat during frying, the frying fat must frequently be replenished, i.e.,the turnover rate is high, and high levels of degradation products do not accumulate. In smaller operations where the frying volume is lower and heating more intermittent, the quality of the fat may become very poor before it is finally discarded. A survey by Thompson et al (1967) of used fats and oils from a number of commercial operations revealed that some fats were of good quality while others had obviously been badly abused before they were discarded.

In countries such as Germany, there are regulations which specify maximum limits of degradation products in used frying fats (Mankel, 1979). In Canada, as yet, there are no regulations concerning quality of used frying fats. Artman (1969) has concluded that a reasonable goal would be to determine which components of frying fats are nutritionally undesirable, to develop methods to determine them, and finally to set reasonable limits for these components in frying fats. However, research has been underway for many years to identify and to determine the nutritional significance of the degradation products in heated fats. As yet, no definite conclusions have been reached.

II. Important Reactions in Frying Fats

Before attempting to review some of the nutritional studies relating to heated fats, a brief review of the terms and methods

more commonly used in the studies will help to clarify the discussion.

There are four main types of degradative reactions which can occur in heated fats: (1) autoxidation, (2) hydrolysis, (3) thermal oxidation and (4) thermal polymerization (Perkins, 1960; Lea, 1965; Chang et al, 1978). The products of thermal oxidation are of most concern in frying fats (Artman, 1969). Autoxidation and especially thermal polymerization are also known to produce nutritionally undesirable components but at normal deep frying temperatures neither of these mechanisms is thought to be of importance.

Determination of the content of oxidized components in heated fats has traditionally depended on two methods: (1) the determination of petroleum-ether insoluble fatty acids and (2) the determination of non-urea adducting fatty acids.

The determination of petroleum ether insoluble fatty acids involves hydrolysis of the fat and extraction of the fatty acids with petroleum ether (Cocks and van Rede, 1966). The oxidized fatty acids are claimed to be insoluble in petroleum ether and can be separated by filtration from the unchanged fatty acids which are soluble. However, the method has received criticism from Artman (1969) who stated that the method is not quantitative as only a portion of the total oxidized fatty acids are insoluble in petroleum ether. Billek et al (1978) have criticized the method for poor reproducibility and accuracy.

The second method, more often reported in nutritional studies is the determination of non-urea adducting fatty acids. This method involves treatment with urea of the total fatty acids freed by hydro-

lysis of the fat. The unchanged fatty acids form insoluble adducts with urea and thus can be separated from the altered fatty acids. The non-adducting fraction can be further distilled to separate the monomeric fatty acid methyl esters (distillable) from the polymeric material (non-distillable) which is thought to consist mainly of dimers and trimers (Kummerow, 1962; Chang et al, 1978). Hence the term distillable non-urea adducting (DNUA) fatty acids which refers to monomeric oxidized fatty acids. The distillable monomeric fraction has also been thought to contain the cyclic fatty acids, i.e., those having ring structure in the carbon chain (Chang et al, 1978). The urea adduction method has often been used to concentrate the cyclic fatty acids for feeding studies (Crampton et al, 1953). This method has also been criticized as not being quantitative. Artman (1969) stated that dienoic fatty acids may not be adducted by urea, and thus they remain in the non-adducting or oxidized fraction. Kummerow (1962) reported that the non-urea adducting fraction of thermally oxidized corn oil contained 9.5% of the total linoleic acid.

III. Nutritional Implications of Heated Fats

The controversy over the nutritional safety of heated fats began back in the early 1950's with the research of Crampton and co-workers. They first observed appetite and growth depression in rats fed heat polymerized linseed oil. Next, they were able to isolate a distillable non-urea adducting (DNUA) fraction from heat polymerized linseed oil which was toxic when fed to rats. The toxic fraction in linseed oil (Crampton et al, 1953) and in soybean oil (Crampton et al, 1956) was thought to be the branched or cyclic

fraction, while the polymeric fraction of these oils was found to be highly indigestible. The research of Crampton et al in 1956 also revealed that sunflower oil, low in linolenic acid, formed a much less toxic "cyclized fraction" than either linseed or soybean oil. From these and following studies the inference seems to have been made that all heated frying fats might contain these toxic components.

However, many other researchers, especially those in the food industry (Rice et al, 1960; Melnick, 1957), felt that this research had little practical significance, as the oils were heated under extreme conditions of high temperature and absence of oxygen which would never be encountered in practical use. Furthermore, linseed oil with its high content of linolenic acid is not normally used as a cooking oil. Numerous studies followed (Rice et al, 1960; Nolen et al, 1967; Poling et al, 1970; Billek , 1979) in which actually used frying fats were fed to rats in long-term feeding studies. Most of these groups were able to demonstrate a slight depression in growth rates and some liver enlargement due to the ingestion of heated fat. But no effects on the health or longevity of the test animals due to the ingestion of heated frying fats as the sole dietary fat source could be demonstrated.

At the same time, Nolen et al (1967) and Perkins and Kummerow (1959) were able to demonstrate the presence of a toxic fraction which could be isolated by distillation from the non-urea adducting fraction of used frying fats or heated fats. As demonstrated by Nolen et al (1967), large doses of the DNUA fraction proved toxic to test animals, but as a component of the unfractionated fat in the

diet, no toxicity symptoms could be noted. Rice et al (1960) were only able to show that the nonadduct-forming fraction from heated oils gave the lowest gains in weight in growth trials as compared to fresh and unfractionated oils, but no toxicity symptoms were evident.

One of the most recent studies by Billek (1979) revealed that the polar or oxidized fraction of a commercially used sunflower oil, when fed as the sole fat source to rats, caused a significant reduction in growth with enlargement of livers and kidneys. Extensive evaluation of the test animals revealed that the oxidized fraction affected metabolic processes in the liver. However, considering (1) that this oil came from the end of a production run when it was discarded, (2) that only the concentrated polar fraction and not the complete heated fat gave a significantly adverse effect, and (3) that these fats were the sole fat source in the diets, the author concluded that there should be no cause for concern about human consumption of heated frying fat.

Research is continuing to identify the suspected toxic compounds in the non-urea adducting fraction of heated fats and to determine their exact effects on metabolism. Gabriel et al (1979) have shown alteration in a number of metabolic processes, caused by the DNUA fraction. However, as in much of the past research, the toxic fractions have been isolated from artificially abused fats, and the argument remains as to whether this has any relation to practical conditions of use in the food industry. Artman (1969) cautions that results from many of the studies could be misleading as the effects observed in the test animals could be due to a de-

struction of essential nutrients in the diet by the oxidized fats.

Some concern has been expressed that the fried foods might preferentially absorb the oxidized components from the frying fat, and that therefore it might be prudent to examine the quality of this absorbed fat. Hussain and Morton (1974) and Alim and Morton (1974) found a greater concentration of oxidized components in the fat extracted from the fried foods than in the frying fat itself. Their conclusions were based on an estimation of oxidized components by urea adduction as well as by column chromatography. However, lack of any statistical analysis makes interpretation of their results difficult, and poor recoveries from the column chromatography method could be contributing to large errors in their reported values. Other reports (Gasparoli and Fedeli, 1980; Alekaev et al, 1979) have not supported these findings.

Artman (1969) concluded that although fats used for frying may lose some of their nutritive value, there is no conclusive evidence that these fats would be toxic in the diet under normal conditions of use. It is most likely, they maintain, that used frying fats would be discarded before they would contain harmful levels of degradation products.

IV. The Use of Canola Oil in Deep Frying

In Canada, the major source of edible oil is now canola, accounting for more than one third of the edible oil consumption (Statistics Canada, 1981). Canola is a relatively new type of rapeseed and reports on the uses of canola oil have hardly kept pace with the rapid improvements made in the oil and the meal. Many of the

past studies have been made with the older varieties of rapeseed oil, while in Canada now only canola (low glucosinolate in the meal, low erucic acid in the oil) is used for edible oil consumption (Vaisey-Genser and Eskin, 1979).

An early study (Dobbs, 1975) reported that rapeseed oil was not as well liked as other oils for frying because of its unpleasant hot oil odour. However, at that time, processors were still using high glucosinolate varieties of rapeseed, and the glucosinolates in the meal had been found to have an effect on the odour of the oil. A more recent report from a major processor of snack foods (Galloway, 1979) revealed that their use of canola oil was limited because the fried products did not have good shelf stability, but there was no mention of odour or flavour problems with the oil. Guillaumin (1979) compared rapeseed, soy and sunflower oils in both heating and frying experiments. Rapeseed oil was similar to soybean oil in amounts of "new chemical compounds" (NCC) formed, while sunflower oil, containing the highest level of linoleic acid of all the oils studied, formed the largest amounts of NCC during both the heating and frying experiments.

Clearly there is a need for information on the performance and stability of canola products, particularly frying fats, under practical conditions of use.

V. Methods for Evaluating Quality of Frying Fats

Over the years, there have been numerous methods used in evaluating the quality of frying fats. Some tests are based on obvious physical changes which occur in the fat during the course of frying,

for example, smoke point, viscosity, colour, and sensory evaluation. There are many chemical tests reported which have been used to determine levels of various chemical compounds found in the fats. Some of the more commonly used chemical tests include determination of free fatty acids, peroxides and hydroperoxides, thiobarbituric acid value, iodine value, and polar components. All of these methods have both advantages and disadvantages; as yet, there does not appear to be an ideal method for evaluation of frying fats.

A. Smoke Point

Smoke point, as determined by the AOCS Official Method Cc-9a-48 (AOCS, 1977) involves heating a specific volume of fat or oil sample at a steady rate of temperature increase until a steady stream of smoke evolves. Since deep frying is carried out at temperatures of around 185^{o}C, the smoke point, ideally, should be well above this temperature and should remain above this temperature during the course of frying.

A smoke point of lower than 170^{o}C together with a content of petroleum ether insoluble oxidized fatty acids of 0.7% or higher are recommended by the German Society for Fat Science as being indicative of severe deterioration in frying fats (Billeck, 1978). Much of the available literature, however, does not appear to support the use of smoke point as an indicator of deterioration in fat. An examination of the data in the literature suggests that most frying fats and oils do have initial smoke points well above normal frying temperature but that they rapidly drop below this temperature during the course of frying when the fats are apparently still of good quality.

Vail and Hilton (1943) and Lowe et al (1958) surveyed a number of fats and oils on the U.S. Market. The smoke points ranged from 174-245° and 177-232°C, respectively, and were correlated negatively with the free fatty acid contents. Fats with high smoke points thus had low free fatty acid contents. Several frying studies have shown that the smoke point rapidly drops below 200°C and often below 170°C after only several hours of frying. Zabik (1962) monitored the smoke points of five identical samples of a vegetable shortening before and after a single frying. The smoke points ranged from 223-232.5°C before frying to 163-182°C after only a single frying when the fats were apparently still of good quality. Vaisey et al (unpublished data) used soybean and canola oils and hydrogenated fats to fry cotton balls for four consecutive 8 hour periods. The smoke points of all fats and oils had dropped below 170°C after 8-16 hours of frying.

The limited usefulness of smoke point for determining quality of frying fat may be due to the method of determining smoke point. The actual determination of the smoke point is a subjective evaluation by the operator. Arens et al (1977) reported a high degree of variability, $\pm$ 25°C, for smoke point determinations in different laboratories. Subsequently, it was demonstrated that the room temperature had a large effect on the smoke point. A modified, more objective method has been published by Bregulla and Seher (1979).

Although smoke point may give an indication of the initial suitability of a fat for frying, it does not appear to be a useful measure of deterioration with the method currently in use. No doubt, an operator will discard a frying fat when it begins to smoke profusely, but it is not clear that this smoke point is at all related

to the smoke point of the same fat as determined by the present official method.

B. Viscosity

Increases in viscosity due to heating of fats and oils have been noted or measured by many researchers. Increase in viscosity due to heating reflects the formation of polymers (Artman, 1969; Sahasrabudhe and Bhalerao, 1963) which has adverse effects on the performance of the frying fat.

Vail and Hilton (1943) noted a viscous gum formation on the sides of containers used for heating fats, although viscosities of the fats were not measured. Lowe et al (1958) also noted this gum formation which was greater for oils than for hydrogenated fats. Stern and Roth (1959) found a strong positive correlation between the viscosity of the fat and the amount of fat absorbed by donuts. They suggested that this could be due to a greater "coating action" of the more viscous fat, as well as a slower rate of heat transfer through the more viscous fat. Many researchers have measured viscosity and found it to correlate well with chemical indicators of fat breakdown, for example, the amount of NUAF material (Rock and Roth, 1966).

Lack of any standardized method for measurement of viscosity makes comparison of results difficult. Methods vary from the use of a steam-jacketed pipette to measure flow rate of fat at 100^{o}C (Rock and Roth, 1966; Stern and Roth, 1959) to the use of viscometers at various temperatures (Thompson et al, 1967; Jacobson, 1967; Chang et al, 1978). However, within one laboratory, with the use of a standardized technique with temperature control,

viscosity measurement might prove a useful quality control test. Viscosity measurements are easily done, and reflect one of the more undesirable changes taking place in the frying fat, namely, the formation of polymeric material.

C. Colour

McGill (1980) suggests the following mechanisms for the development of colour in used frying oils and fats: (1) oxidative reactions of the oil which result in the formation of coloured compounds, (2) the loss of soluble caramel-coloured compounds from the fried food into the fat and (3) the presence of finely divided carbon, or charred food particles, in the fat. Fritsch (1981) reported a greater increase of colour in fats when they were used for frying potatoes than when they were only heated; this was believed to be due to leaching of browning pigments from the food into the fat.

Colour values of a fat can easily be measured by any available colorimeter such as the Lovibond tintometer (Hussain and Morton, 1974). However, due to the many factors which can influence the colour of a fat, the actual colour values are meaningful only in the study of a particular fat and frying operation.

D. Sensory Evaluation

Sensory evaluation is the most commonly used method for evaluating the quality of frying fats and especially the fried products. Unfortunately, it is the method on which the least information is available.

In most small commercial operations and in the home, this is

the only method by which the user decides when to discard the frying fat. The decision is based on a combination of odour evaluation, visual assessment of the amount of smoke, and evaluation of the flavour, texture and appearance of the fried product. Billek et al (1978) acknowledge the primary importance of sensory evaluation in assessing fat deterioration and states that analytical data should be used to support the findings of a sensory panel. However, there have been few studies published in which sensory evaluation has been correlated to other physical or chemical indicators of deterioration.

The amount of time required to train a sensory panel, the effort required to maintain and motivate the panel, and the high degree of variability of panel results (Dobbs, 1975) are some major reasons why only limited sensory evaluation has been conducted.

The level of free fatty acids (FFA) in a frying fat is often used as a measure of deterioration and as an indicator of when to discard fat in large commercial operations (Galloway, 1979), but there is little information available as to the effect of free fatty acids on flavour or quality of the fried products. Hoffman (1962) states that FFA containing 16 or 18 carbon atoms have little effect on flavour, while FFA containing 14 or fewer carbon atoms, for example, from coconut and palm kernel oils, may give distinct 'off' flavours. A study by Hartman et al (1975) supports this statement. They added increasing levels of endogenous FFA back to four different types of fats and oils and determined the minimum detectable levels for each by flavour evaluation. In groundnut and soybean oils, the minimum amount detectable was 1.5% FFA, while in babassu oil

(an oil similar to coconut oil) as little as 0.1% FFA was detectable. However, these oils were not heated and it may be that heating would alter these effects of FFA on flavour.

Odumosu et al (1979) compared sensory and chemical methods of evaluating thermally oxidized groundnut oil; however, the temperature of oxidation was 100°C which is less than frying temperature. They found good correlation between sensory flavour scores and chemical indicators of fat deterioration.

E. Free Fatty Acid Value

The free fatty acid value is a measure of the free or non-esterified fatty acids in the fat, indicating the degree of hydrolysis of the fat. Free fatty acid values are reported in most studies on frying fats and are often the sole method of quality control in large frying operations (Galloway, 1979).

Although free fatty acid values are widely reported as an indicator of breakdown in frying fats, it is not clear which effects the free fatty acids themselves have on the quality of the fat. Fritsch (1981) criticizes the method as it does not distinguish between free fatty acids produced by hydrolysis, which have little effect on nutritional or sensory quality of the products, and free fatty acids produced by oxidation, which do have detrimental effects on both. As shown by Hoffman (1962) it is the carbon chain length of the free fatty acids more than the actual amounts which has the greatest effect on flavour of unheated fats.

All studies in which free fatty acids were measured show an increase in free fatty acids during frying or heating and a good

correlation of these values with other chemical indices of deterioration. The measurement of free fatty acids can be done easily in any quality control laboratory, and this fact has no doubt contributed to its wide use an an indicator of quality.

The most widely used method is a titration with NaOH (AOCS method Ca-5a-40, AOCS, 1977). A more recent method (Lowry and Tinsley, 1976) involves a colorimetric determination. The fat or oil sample is mixed with cupric acetate reagent and coloured complexes are formed by the copper ion and free fatty acids. This method has the advantages of requiring much smaller samples and less time than the titration procedure.

F. Peroxides

Hydroperoxides and peroxides are the initial products formed during the oxidative deterioration of fats and oils (Artman, 1969). The peroxide value is often used as a measure of deterioration in unheated fats and oils (Gray, 1978). However, the method has been criticized by many researchers (Artman, 1969; Fritsch, 1981; Kantorowitz and Yannai, 1974) for use with heated fats as the peroxides quickly decompose at frying temperatures. Peroxide value is most commonly estimated by measuring the amount of iodine formed from a potassium iodide solution added to the fat (Cocks and van Rede, 1966). Gray (1978) has summarized the various procedures used for determination of peroxide values and the possible sources of error associated with each method.

G. Iodine Value

The change in iodine value due to heating of a fat or oil reflects the loss in double bonds which has occurred in various degradative reactions (Artman, 1969). Iodine value is defined as the amount of iodide removed from a solution of potassium iodide by reaction at the site of the double bonds (Cocks and van Rede, 1966).

H. TBA Value

The thiobarbituric acid (TBA) test for determination of malonaldehyde, a secondary oxidation product, has often been used as an indicator of the extent of lipid oxidation (Gray, 1978). Jacobson (1967) used the TBA test to monitor the quality of fresh frying fats and the stability of fried products, but not the quality of fat during frying. Artman (1969) questions the use of the TBA test with heated fats as it has been reported that malonaldehyde is volatile at frying temperatures.

The amount of malonaldehyde is estimated by a colormetric reaction in which two molecules of thiobarbituric acid react with one molecule of malonaldehyde (Gray, 1978).

I. Polar Components

The term polar components in fats is generally used to describe a wide range of chemical compounds formed by breakdown of the triglyceride molecules. The triglyceride molecules are relatively non-polar while the degradation products are more polar due to the presence of hydroxyl and other polar groups. This difference in polarity has been the basis for a number of chromatographic methods

for estimating the total polar components in a fat or oil. Since determination of the total polar components gives an absolute measure of the amount of deterioration which has taken place in the fat, it appears to be a useful method for determining the life of the fat (Billek et al, 1978).

There are several possible methods for determining total polar components in fats.

1. Change in Dielectric Constant

The Foodoil Sensor was recently introduced to the market as a portable instrument which gives a measure of the dielectric constant of an oil or fat. Since the dielectric constant changes as additional polar groups are formed, this measurement could give a quick estimation of polar components in the fat. Very little skill is required to operate the instrument as it requires only a small sample of the melted fat or oil to be placed in the sample cup and a reading to be taken. Graziano (1978) indicated good correlation of Foodoil Sensor readings with results of other chemical tests of fat deterioration. However, more extensive testing by Paradis and Newar (1981) showed the instrument to be highly affected by the presence of water or food fat in the frying fat sample. Values from the Foodoil Sensor were not meaningful for use in comparing deterioration among different fats or oils. These problems were also found by Fritsch (1981).

2. Column Chromatography

Billek et al (1978) compared two column chromatographic methods with the method for "petroleum ether insoluble fatty acids", a standard method used by the German Society for Fat Research for

determination of fat quality in commercial operations such as restaurants. An automated liquid column chromatographic system using a flame ionization detector proved to be rapid but the reproducibility was not as good as with a manual column chromatographic method with weighing of the eluted fractions. This latter method was less costly in terms of equipment but required more time for each analysis. With this method, a sample of the frying fat, dissolved in a solvent, is loaded onto a silica gel column. The non-polar or triglyceride fraction is eluted first from the column with a non-polar solvent. The polar fraction is more strongly adsorbed on the column packing and is subsequently eluted with a more polar solvent. Both fractions can be determined gravimetrically. Billek et al (1978) were able to correlate the value of 1% of petroleum ether insoluble fatty acids in the fat, indicative of severe deterioration, with a value of 28% of polar components as determined by column chromatography. In a later study (Billek , 1979) a value of 30% polar components was confirmed to be indicative of severe deterioration, based on accompanying sensory evaluation and other analytical data.

Paradis and Newar (1981) compared the column chromatography method of Billek et al (1978) with several other methods, i.e., the determination of peroxide value, TBA value, free fatty acid value, dielectric constant, and contents of triglyceride dimers determined by gas chromatography. The column chromatography method was found to be time-consuming, but also the most sensitive to changes in the oil.

Guillaumin (1973) reported a similar method of column chroma-

tography for determination of "new chemical compounds" (NCC) in heated fats. The heated fats were hydrolyzed and the fatty acids converted to methyl esters, and chromatographed on a hydrated alumina column. The unchanged fatty acid methyl esters were eluted first with hexane and the more polar compounds subsequently with a series of solvents of increasing polarity. Recoveries from the column were stated to be better than 99%, and the reproducibility of results was $\pm$ 5%. The levels of NCC in unheated oils ranged from 2-4% and increased to 6-10% after the oils had been used to fry 20 lots of french fries over a period of 20 days. There were no other chemical or sensory tests done to indicate the degree of deterioration of the oils.

3. Thin-Layer Chromatography with Flame Ionization Detection

Thin-layer chromatography on quartz rods coated with silica gel (chromarods) followed by scanning of the rods with a flame ionization detector is a relatively new concept in quantitative thin-layer chromatography. The Iatroscan Analyzer was developed by Iatron Laboratories Inc. of Japan following successful development of reusable chromarods. The Iatroscan thin-layer chromatography flame ionization detection (TLC-FID) system and its use have been described and reviewed in detail by Ackman (1981).

Separation is accomplished on chromarods which can be mounted in sets of ten in a metal frame as shown in Fig. 2. Following sample spotting and development, as in conventional thin-layer chromatography, the frame containing the chromarods is placed in the scanning assembly of the instrument (Fig. 3). The rods are automatically and sequentially passed through the flame of a hydrogen

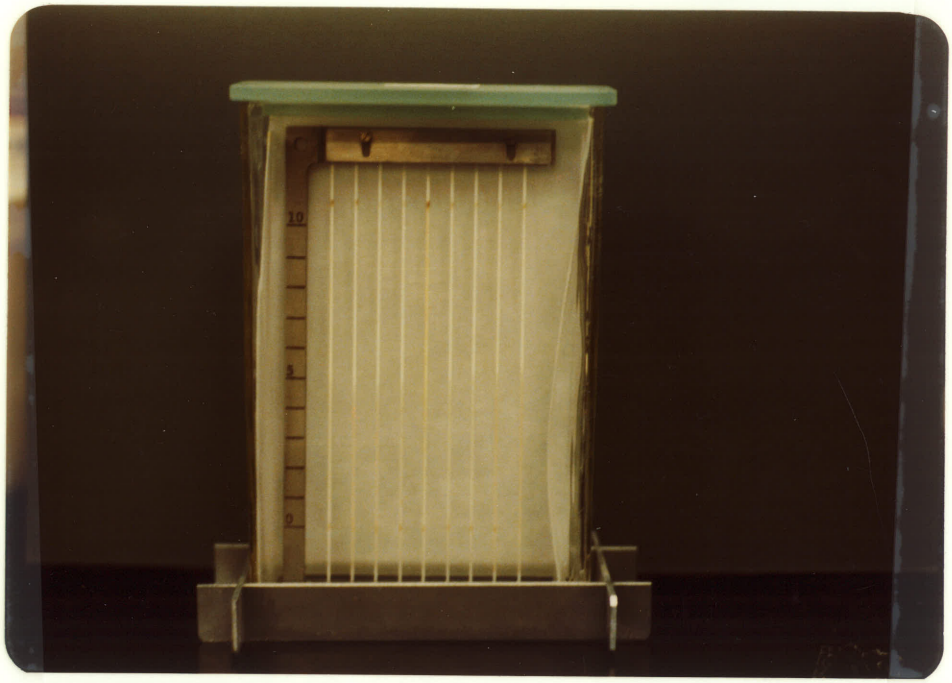

Figure 2: Chromarods mounted in the development/scanning frame in the development tank.

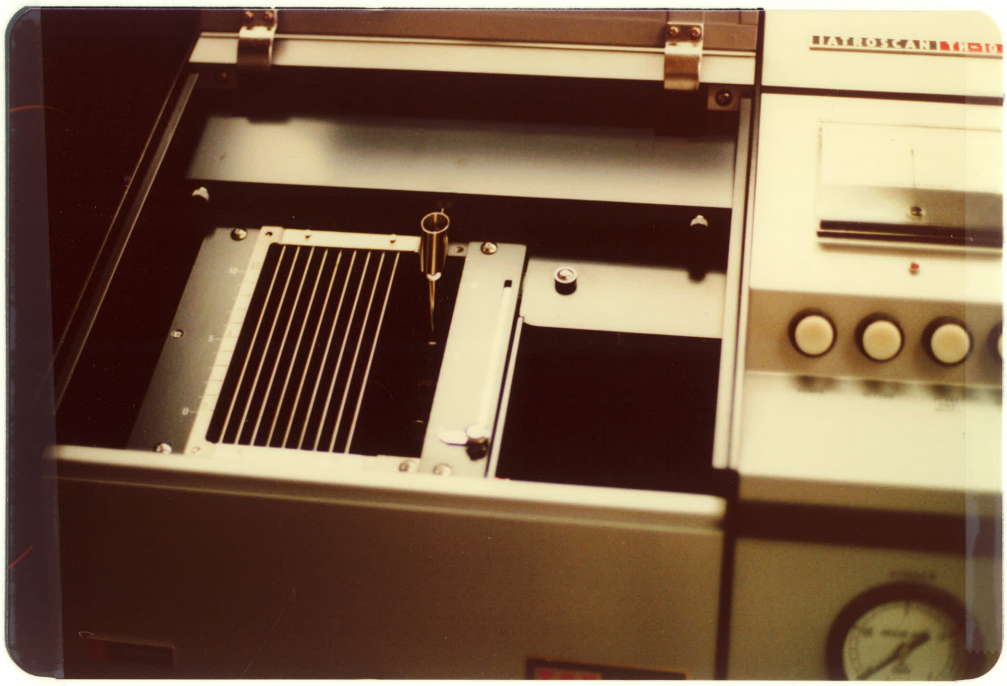

Figure 3: Frame with chromarods in the scanning assembly of the Iatroscan to the left of the cylindrical-shaped ionization detector.

flame ionization detector which quantitatively estimates the amount of substance on the rods while at the same time cleaning and reactivating the rods. Following scanning, the clean and reactivated rods are again ready for use.

Several researchers have reported the use of the Iatroscan TLC-FID system for quantitative separation of lipids (Innis and Clandinin, 1981; Kaitaranta and Ke, 1981; Hirayama and Morita,1980; Kaitaranta, 1980; Kramer et al, 1980, Bradley et al, 1979; Mills et al, 1979; Tanaka et al, 1979; Vandamme et al, 1978). There has been little application of the TLC-FID system in areas of food lipid analysis. Kaitaranta and Ke (1981) have described the use of the Iatroscan to measure changes in polar lipid content of fish oils. They compared polar lipid content determined by TLC-FID to thiobarbituric acid (TBA) values and to increases in weight of oil samples due to oxygen uptake. They found a significant linear correlation (r=0.945) between the polar lipids estimated by TLC-FID and the weight gain, and also between polar lipids and TBA values (r=0.935).

Regardless of the class of compound to be quantitatively analyzed, there are several important variables to consider when using the TLC-FID system.

Quantity of sample for spotting. The flame ionization detector is sensitive to very small amounts of material, less than 1 µg (Kaitaranta and Nicolaides, 1981); however, Ackman (1981) reports that the most commonly used amounts for spotting are in the range of 3-30 µg. The sample of material is spotted in a volume of 1-2 µl of solvent; this is applied to the rod in small aliquots of 0.2 to

0.5 µl, allowing the solvent to dry between applications to prevent excessive spreading of the material at the origin.

Solvent development system. Selection of a suitable solvent development system may require some experimentation. Kramer et al, (1980) studied the effects of solvents on the resolution of neutral lipids on chromarods and concluded that the TLC-FID system is unique, and therefore the solvent systems used in conventional TLC may not necessarily be successful with chromarods. They found that very small changes in composition of the developing solvents affected lipid resolution, and also noted that the resolution decreased as the rods aged. Ackman (1981) has summarized all of the various solvent systems for chromarod development which have been reported.

Mills et al (1979) have suggested that during development of lipids, material is progressively "lost" as it migrates up the chromarod. Standardization of solvent system and especially of developing times are therefore extremely important.

Many researchers (Kaitaranta and Ke, 1981; Innis and Clandinin, 1981; Sipos and Ackman, 1978; Vandamme et al, 1978) have reported developing times rather than solvent front height, as it is often very difficult to see the solvent front on the chromarods. Solvent front heights are often reported when the rods are partially developed first in one solvent system and then in another to complete the separation (Mills et al, 1979).

It has also been noted (Ackman, 1981; Hirayama and Morita, 1980) that all chromarods do not have identical developing rates. The rods should initially be checked, either in the developing solvent or by

development of standards, and grouped in sets of ten rods, all of which should have similar developing rates.

Operating variables of the Iatroscan Analyzer. The three variables to consider in the operation of the flame ionization detector system are (1) hydrogen flow rate and (2) air flow rate to the burner and (3) scanning speed of the rods as they are passed through the flame.

The manufacturer recommends a hydrogen flow rate of 160 ml/min which should correspond to an instrument pressure gauge setting of 1.2 kg/cm^2. However, there is a great deal of discrepancy between this recommendation and results reported elsewhere. Several studies have reported hydrogen pressures of 0.7 kg/cm^2 (Vandamme et al, 1978; Kairatanta and Nicolaides, 1981) and 0.75 kg/cm^2 (Sipos and Ackman, 1978), with no mention of the flow rate corresponding to this pressure. Others have reported only the flow rates, 80 ml/min (Innis and Clandinin, 1981) and 188 ml/min (Bradley et al, 1979) with no mention of the corresponding hydrogen pressures. A study reviewed by Ackman (1981) stated that a hydrogen flow rate of 160 ml/min corresponded to a pressure of 2.0 kg/cm^2. Since Ackman (1981) reports that the hydrogen flow rate may affect both the magnitude and the reproducibility of the FID response, it would appear to be important to select a rate which gives the most reproducible response.

The manufacturer recommends an air flow rate of 2000 ml/min which can be set directly on the instrument flow meter. There are no reports of the air flow rate having any effect on the response

and it is usually left at the recommended rate.

The scanning speed of the rods is varied by changing speed ratio gears on the carriage of the scanning assembly. The manufacturer does not recommend a specific scanning speed, but rates of 2.3, 3.1 and 4.6 cm/sec (representing scanning gears no. 40, 30 and 20, respectively) have most often been reported (Ackman, 1981). The manufacturer cautions that at slower scanning speeds, it may be necessary to reduce the hydrogen flow rate to avoid over-heating and thus shortening the life of the chromarods. Thus, it may be necessary to try several combinations of hydrogen flow rates and scanning speeds as reported by Bradley et al (1979) in order to find the most reproducible response.

Flame ionization detector response. Having considered the previously mentioned variables, the final variable to consider is the response of the flame ionization detector to the substance or substances under investigation. Most researchers have found the detector response to be linear for amounts of material ranging from 1-30µg for any particular class of lipid (Ackman, 1981). However, more researchers have also found that the response differs for different classes of lipids which necessitates the use of response factors or correction factors in order to accurately quantitate the results.

Several methods have been suggested for the calculation of correction factors, but the most logical method appears to be the determination of a calibration curve for each component of interest as described by Mills et al (1979). They determined the detector

response for amounts of each component ranging from 1 to 30 µg (Fig. 4). A regression line was estimated for each component following the method of least squares. From the peak height and regression lines, they were able to calculate the corresponding weight for each component of an unknown mixture.

Mills et al (1979) further reported on a decrease in reproducibility of the peak heights when a substance was chromatographically developed along the rod before being scanned, rather than being scanned at the point of origin, before development. Thus, a coefficient of variation of 19.6% was obtained for a cholesterol stearate standard after development and scanning; this was considered to be due to inconsistent behaviour of the individual chromarods. A much lower coefficient of variation, 6.1%,was obtained when samples of cholesterol stearate were spotted and scanned without chromatographic development.

However, the opinion of most researchers who have used the TLC-FID system is that, in spite of poor reproducibility, it is a quick and sensitive method for both qualitative and quantitative analysis of mixtures, particularly for lipids,for which it has been most widely used.

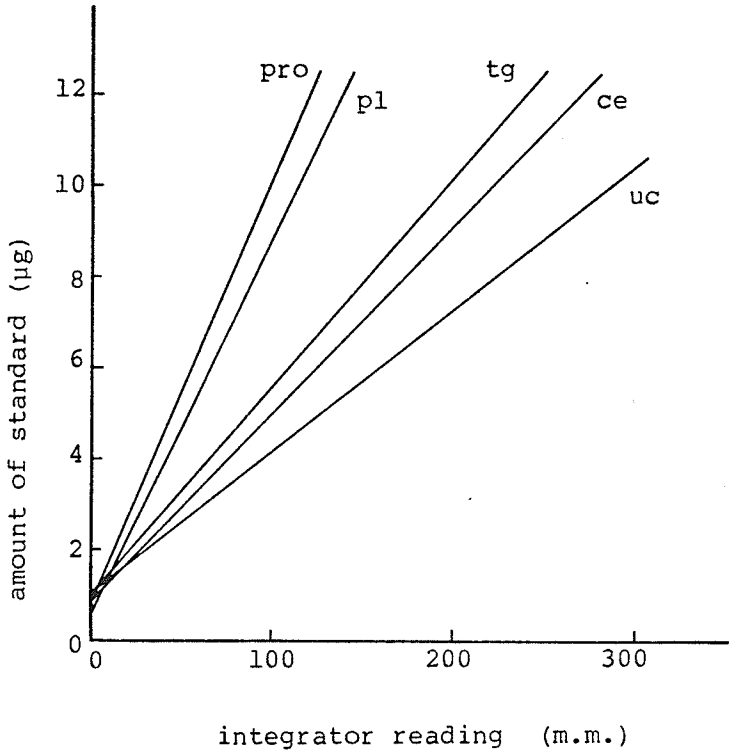

Figure 4: The relationship between the weight of substance applied to the chromarod and its response in the flame ionization detector after chromatographic development. Straight lines were fitted to the data by the method of least squares. Ce, cholesterol esters; uc, unesterified cholesterol; tg, triglyceride; pl, phospholipid; pro, protein (from Mills et al, 1979).

MATERIALS AND METHODS

I. Preparation and Collection of Used Frying Fats

The following three brands of commercial frying fats (heavy duty hydrogenated) were used in the study:

1. Chipper Biscot - a hydrogenated canola oil (variety Tower) from Canada Packers (iodine value = 78).

2. Tasty Fry - a hydrogenated canola oil from Canbra Foods Ltd. (iodine value = 76).

3. Hydrogenated soybean oil - from Proctor and Gamble Co. (iodine value = 76).

Each of these fats was used in turn for frying frozen french fries (McCains 3/8" regular cut institutional pack) for a period of five 8-hr days. Each morning, the fat in the fryer (Garland Model 80-03 institutional electric deep fryer) was heated to 185^{o}C (375^{o}F) and 910 g (2 lb) lots of the frozen fries were cooked for 3 min at 15 min intervals throughout the day. A total of 30 lots (30x190 g = 27.3 kg) were fried each day. After the 15th and 30th frying of each day, the fryer was topped up with freshly melted fat to replace that lost by absorption and sampling. Approximately 1200 g or 10% of the total weight of the fat was added at each topping up.

Samples of both the frying fat and the cooked french fries were obtained at intervals throughout each of the 5 days of frying (Fig. 5). The fat and the french fry samples were placed in glass and plastic containers, flushed with nitrogen, and placed in frozen storage (-25^{o}C) until further analysis could be done.

Time	Fry No.	Sampling Schedule		
		Frying Fat Sample *	French Fry Sample **	
8:15 A.M.	0	*		Fat heated to 185°C
8:30	1			
	2			
9:00	3		**	
	4			
9:30	5			
	6	*	**	
10:00	7			
	8			
10:30	9		**	
	10			
11:00	11			
	12	*	**	
11:30	13			
	14			
12:00	15		**	Fryer topped up with fresh fat
	16			
12:30 P.M.	17			
	18	*	**	
1:00	19			
	20			
1:30	21		**	
	22			
2:00	23			
	24	*	**	
2:30	25			
	26			
3:00	27		**	
	28			
3:30	29			
	30	*	**	Fryer topped up,
4:00				Fryer turned off for the night

Figure 5: Daily frying and sampling schedule.

All samples were coded with 4-number, hyphenated codes (e.g., 1-1-30-1) where the first number (1-3) indicates the fat type (cf. p. 31) the second number (1-5) indicates the day of frying, the third number (1-30) indicates the fry number, and the fourth number (1 = fat; 2 = french fries) indicates the product. Thus, for example, code 1-1-30-1 would indicate Chipper biscot frying fat - day 1 of frying - fry number 30 - frying fat sample.

II. Analysis of Frying Fat and French Fry Samples

Samples of (1) the frying fats and (2) the fats extracted from the french fries were subjected to a number of analyses. Those which were done by the author are reported in detail in the following section and others are referred to in the manuscript in the appendix.

(1) The frying fat samples were filtered through glass wool at the time of sample collection to remove charred food particles. At the time of analysis, the samples were melted at 55-60^{o}C prior to weighing.

(2) The fat in the french fries was extracted prior to analysis by the method of Bligh and Dyer (1959) using chloroform: methanol: water (1:2:0.8 v/v). Additional volumes of chloroform and water were added to form a biphasic mixture (chloroform: methanol: water, 2:2:1.8 v/v) from which the chloroform could be separated from the methanol: water phase. This extraction procedure was carried out in the Department of Foods and Nutrition.

A. Free Fatty Acids

The free fatty acid contents in the samples of frying fats and the fats extracted from the french fries were determined colorimetrically according to a method by Lowry and Tinsley (1976) as adapted by J.K. Daun (personal communication).

Approximately 200 mg of the pre-melted fats were weighed into 10 ml screw top test tubes, and 5 ml of toluene was added to each tube, followed by 1 ml of cupric acetate reagent (5% w/v aqueous). The tubes were capped, shaken for 1 min and then mixed on a Vortex mixer for 15 sec to complete mixing. The tubes were centrifuged at 3000 rpm for 5 min and the upper, clear layer of each tube was carefully pipetted into a test tube. The samples were then aspirated directly into the spectrophotometer (Beckman Model 25) cuvette; the absorbances were read at 715 nm. The percentage of free fatty acids was determined from an absorption calibration curve for oleic acid standards (Fig. 6).

B. Polar Components

1. Change in Dielectric Constant

Changes in dielectric constant of frying fats were measured with the Foodoil Sensor (Northern Instruments Corp., Minnesota).

Samples were melted in small beakers prior to being placed in the sample cup of the Foodoil Sensor. A pipette was used to place approximately 0.5 ml of melted fat in the sample cup. When the sample had reached the proper temperature as indicated by a green light on the instrument panel, the test button was depressed and the deflection

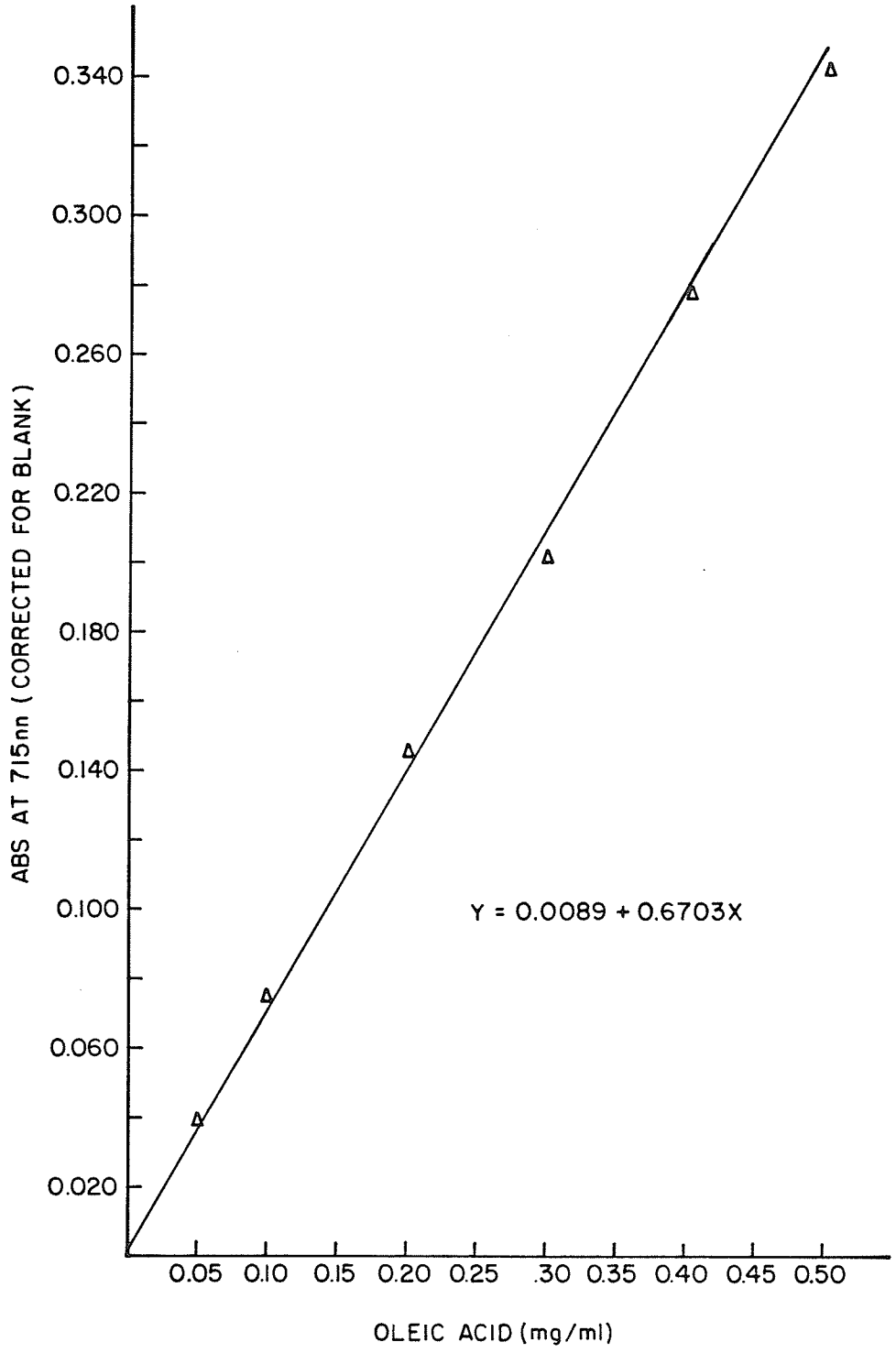

Figure 6: Absorption curve and regression line for oleic acid standards.

of the needle was observed. The sample cup was emptied, wiped clean, and the next sample read following the same procedure.

An unheated fat sample was initially used to calibrate the instrument to zero deflection, after which the heated fat samples were sequentially tested. Only preliminary test fats and not the experimental samples were tested using the Foodoil Sensor.

2. Column Chromatography

Separation using a 25 g silica gel column. Total polar components in the fats were determined by column chromatography as described by Billek et al (1978). Silica gel (60-200 mesh, Davidson Co.) for the columns was activated by drying at 160°C for 4 hr; then water (5% of the weight of the silica gel) was added and the mixture shaken for 1 hr to equilibrate. Twenty-five grams of the activated silica gel was used for each column.

A glass column (38 cm x 2.1 cm i.d.) with a sintered glass disc support and Teflon stopcock was partially filled with 50 ml of solvent A (petroleum ether: ether, 87:13 v/v). A disc of fiberglass filter paper was fitted over the sintered glass disc to retain the fine particles of the silica gel. Originally, a wad of cotton wool or glass wool was used to cover the glass disc (as described by Billek et al (1978). However, the glass wool did not always completely retain the silica gel, and it was difficult to obtain level packing of the silica gel on top of the wad of glass wool. The disc of fiberglass filter paper was more effective than the glass wool in both of these respects.

The 25 g of silica gel was slurried in 80 ml of solvent A in a small beaker and was stirred to remove air bubbles. The slurry was

gradually poured through a glass funnel into the column. The stopcock of the column was left partially open during the packing procedure to facilitate even packing of the silica gel. Additional solvent A was used to rinse the remaining silica gel from the beaker and the funnel into the column.

Several techniques were tried to obtain an even packing of the column. It was necessary to maintain a continuous flow of the slurry into the column to avoid channeling. Also, much difficulty was encountered in having the silica gel settle without the formation of air bubbles which tended to migrate and form large breaks or channels in the column. An electric vibrator was used to improve the settling of the silica gel in the column. Finally, when the silica gel was settled in the column, a small disc of fiberglass filter paper was placed on top to prevent disturbance of the surface of the silica gel when adding sample and eluents.

A sample of the melted frying fat (1 g weighed to four decimal places) was weighed into a small beaker and dissolved in 10 ml of solvent A. The solution was carefully added to the top of the column, followed by two 5-ml aliquots of solvent A used to rinse the beaker.

The triglyceride (non-polar) fraction was eluted with 150 ml of solvent A followed by the polar fraction with 150 ml of solvent B (diethyl ether). The flow rate was 2.5 ml/min, controlled by partially closing the stopcock of the column. Twelve fractions (25 ml each) were collected in graduated cylinders and transferred with rinsing into pre-weighed 100-ml round bottom flasks. The solutions were evaporated to dryness with a rotary evaporator and a waterbath ($60^{o}C$);

followed by heating in an oven (110°C) for 4-5 min to remove the last traces of solvent. The flasks were placed in a desiccator to cool, and were then weighed. The weights of the first 6 fractions eluted with solvent A were added to determine the total weight of non-polar material, and the weights of the last 6 fractions eluted with solvent B were added to determine the total weight of polar material. The recovery of sample from the column was calculated as the combined weight of all eluted fractions as a percentage of the weight of the sample charged to the column.

Attempted reconditioning of the column between samples. A new 25 g column was used to fractionate a 1 g sample of used frying fat. Following elution, the column packing was washed with 60 ml of solvent A. A second 1 g sample of fat was fractionated as described in the previous section. The column packing was successively washed with 60 ml of methanol, 60 ml of acetone, and 60 ml of solvent A. A third 1 g sample of the same fat was fractionated on the washed column.

Separation using a 6.25 g silica gel column. The complete procedure for the 25 g column was reduced to one-quarter scale. A column (30 cm x 1 cm i.d.) was packed with 6.25 g silica gel. A 250 mg sample of frying fat was eluted from the column, with 50 ml of solvent A followed by 50 ml of solvent B. Initially, twenty 5-ml fractions were collected. Once the pattern of elution was established, only two bulk 50 ml fractions were collected and weighed.

Difficulties were still encountered in obtaining uniform packing

in the column, which appeared to be temperature related. This problem was finally solved by putting a circulating water jacket on the column, and circulating cold tap water throughout the procedure. This completely eliminated the problem of bubbles and channel formation in the column and greatly increased the flow rate.

Analysis of frying fats. Samples of the unheated frying fats and the heated fats from the 30th fry of each of the 5 days for all three types of fat were fractionated on either a 25 g or a 6.25 g silica gel column.

3. Thin Layer Chromatography with Flame Ionization Detection by an Iatroscan Analyzer

Since quantitative thin-layer chromatography on chromarods is a relatively new procedure, there were no established methods to follow for separation of heated frying fats. A method for the separation of heated frying fats into non-polar and polar fractions was developed as follows:

Selection and activation of chromarods. Ten chromarods (type S, Technical Marketing Associates, Mississauga, Ontario) were secured in the dual purpose development/scanning frame (Technical Marketing Associates). They were simultaneously cleaned and activated by passage through the flame ionization detector of the Iatroscan Analyzer (Model TH-10, Technical Marketing Associates). Between periods of use, the chromarods were stored in a glass tank containing distilled water. Just prior to use, the rods were removed, dried 5 min in an oven at 105^{o}C and scanned through the flame detector.

In order to check the similarity of developing rates of the

10 rods, they were developed in solvent (petroleum ether: ether, 87:13 v/v) for 17 min and the heights of the solvent fronts on each rod were compared. As the 10 rods appeared to have similar developing rates, no further selection of chromarods was required.

Application of samples to the chromarods. Fat samples were dissolved in chloroform (distilled in glass) and applied in small portions to the origin of each chromarod. Spotting of volumes of more than 1 µl was done with a 10 µl syringe (Unimetrics Syringe, Model TP5010 TLC) which had a Teflon tip especially for spotting in thin-layer chromatography. This eliminated the danger of scratching the fine silica coating on the rods, and helped to prevent solvent from creeping up on the outside of the syringe needle during application. Spotting of samples of less than 1 µl was done with a 1 µl syringe.

Initially, samples of concentrations from 1 to 10 µg / µl were spotted in volumes ranging from 0.5 to 6 µl . It was found suitable, later, to standardize on a sample concentration of 10 µg / µl , and to spot a volume of 2 µl , thus depositing a sample of 20 µg on the rod. The 2 µl of solution was spotted in small aliquots of approximately 0.5 µl , allowing the solvent on the rod to dry between each application.

Solvent system and development procedure. A mixture of petroleum ether (bp 30-60^{o}C) and diethyl ether (85:15 v/v) gave adequate resolution of the triglyceride fraction from the polar material. Decreasing the amount of diethyl ether in the mixture (pet. ether: ether, 87:13 v/v) allowed the polar fraction to remain as one peak near the origin, but did not always adequately resolve the triglyceride peak. Increasing the amount of diethyl ether (pet. ether: ether,

80:20 v/v) gave very good resolution of the triglyceride peak but caused the polar fraction to be resolved into several smaller peaks which were more difficult to accurately quantitate.

The rods were developed for 17 min in 60 ml of pet. ether: ether (85:15 v/v) in a chromarod tank lined on three sides with filter paper. The frame containing the rods was removed from the tank and dried in an oven at 105^{o}C for 5 min to remove any traces of solvent.

Operating conditions of the Iatroscan Analyzer. The hydrogen pressure and air flow rate were initially set at 1.2 kg/cm^2 and 2000 ml/min. The rods were traversed through the flame at a rate of 0.3 cm/sec (i.e., 40 sec per scan), using gear no. 30 on the scanning frame drive. The amplifier output was set at maximum. The analog signal cable from the detector was connected to a digital integrator (Autolab, Model 6300-12) to which was connected a potentiometric recorder (Beckman, Model 1005). The external chart feed cable from the Iatroscan Analyzer was coupled directly to the recorder; this activated the pen and chart paper drive only during each scan. This offered a considerable saving in chart paper as the chart paper drive was disengaged during the return of the frame between scans. The recorder was operated at 100 mv with a chart speed of 5 in/min.

Several combinations of hydrogen flow rates (1.0, 1.2 and 1.4 kg/cm^2) and scanning speeds (0.3 cm/sec and 0.4 cm/sec) were tested to determine which conditions gave the most reproducible response.

Determination of linearity of response and relative response. Standard solutions of a triglyceride fraction and a polar fraction

isolated by column chromatography from a heated fat (code 2-5-30-1) were each made up at concentrations of 5 µg/µl and 1 µg/µl in chloroform in 25ml glass stoppered volumetric flasks. Volumes of 0.5 to 6.0 µl of the standard solutions (i.e., 1.0 to 30 µg) were spotted on each of 9 rods, developed and scanned. The integrated peak areas were used to determine (1) the linearity of detector response for each of the two classes of compounds over a range of sample sizes and (2) the response for the triglyceride fraction relative to the polar fraction. The detector response was also determined for a pure triglyceride (triolein, Supelco Co.).

Separation of mixtures of non-polar and polar material of known composition. Using triglyceride and polar fractions isolated by column chromatography from a heated fat (code 2-5-30-1), a series of mixtures were prepared with the following compositions:

Concentration (in $CHCl_3$) 10 µg/µl	Triglyceride Fraction (% by wt)	Polar Fraction (% by wt)
"	65.57	34.43
"	70.17	29.83
"	75.47	24.53
"	79.90	20.10
"	85.71	14.24
"	90.91	9.09
"	95.21	4.79

These solutions were individually spotted on each of 9 rods (2 µl/rod), developed and scanned as previously described.

Analysis of heated frying fats. Samples of frying fats from the beginning and end of each frying period for each of the three brands of fats were made to a concentration of 10 µg/µl in chloroform.

Each of the solutions was spotted on 9 replicate chromarods (2 µl/ rod), which were developed and scanned as previously described.

RESULTS AND DISCUSSION

Free fatty acid values, determined by a rapid colorimetric method, were done on frying fats and fats extracted from the french fries. Three different methods for estimation of total polar components were evaluated; change in dielectric constant as measured by the Foodoil Sensor, gravimetric determination of polar components by liquid column chromatography, and a quantitative thin-layer chromatographic technique using the Iatroscan Analyzer.

A. Free Fatty Acids

Free fatty acid measurements were done in duplicate on samples of frying fat from fry no. 0, 6, 18, 24 and 30 of each of 5 days for all 3 types of fat. Results were expressed as % of free fatty acids (as oleic) determined from the regression equation for oleic acid standards (Fig. 6, p. 35). The mean values for each fry over 5 days of frying for all 3 fat types are shown in Fig. 7. The free fatty acid values appear to parallel very closely the changes taking place in the frying fat. The levels of free fatty acids increased each day, but decreased after the 15th and 30th fry of each day when the fryer was topped up with fresh fat as would be expected. Mean values ranged from 0.01 to 0.04% for the unheated fats to 1.11 to 1.26% for the fats after 5 days of frying. The soy frying fat initially had the lowest free fatty acid value (0.01%) but throughout the frying it had the highest levels of free fatty acids. The two canola fats had similar levels of free fatty acids throughout the five

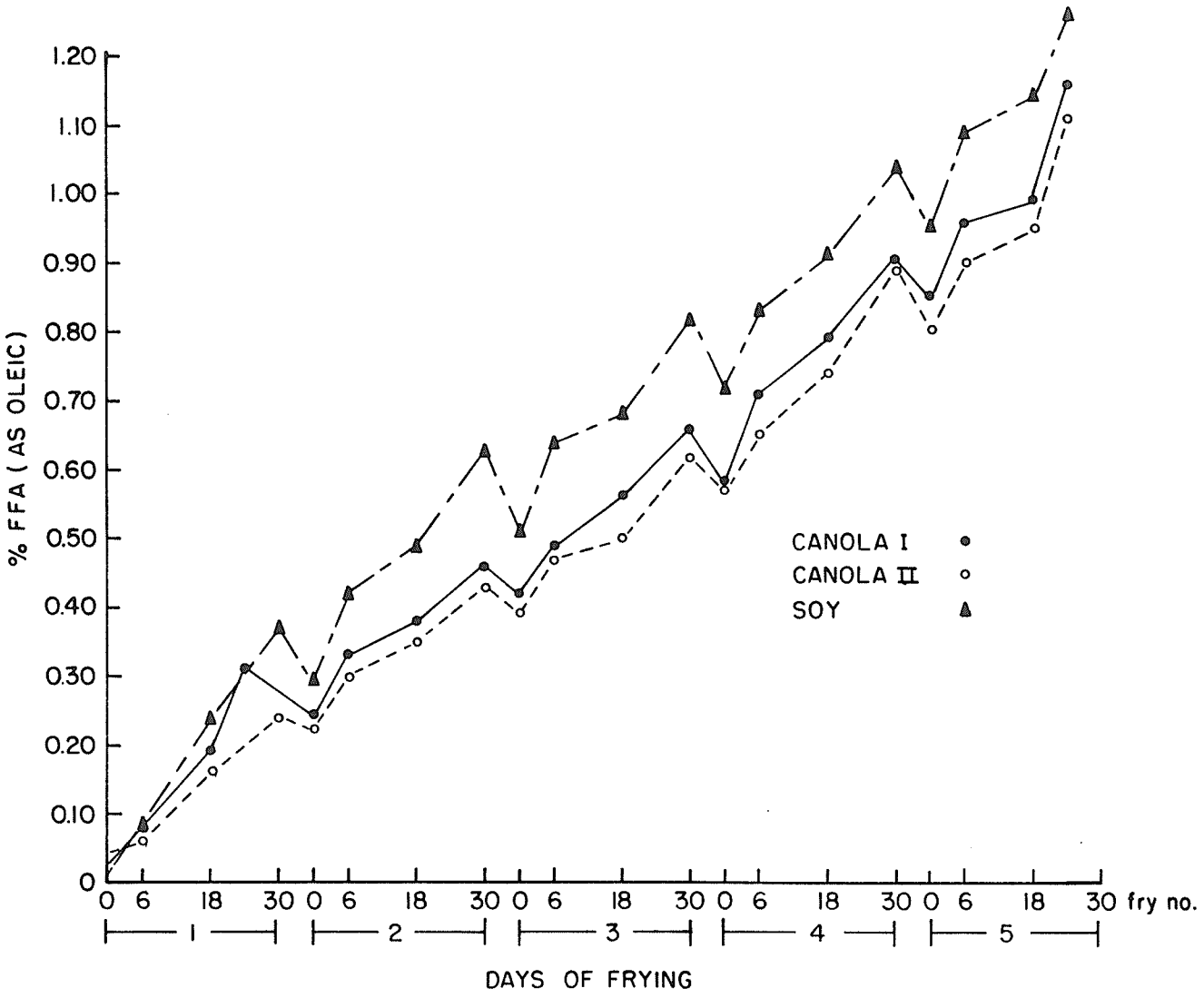

Figure 7: Free fatty acid values of three types of fat over five days of frying.

days of frying.

Correlations of the free fatty acid values with hours of frying for the 3 fats are detailed in the appended manuscript. In brief, there were high correlation coefficients for the increase in free fatty acid value with increase in hours of frying for all 3 fats.

Free fatty acid values for the fats extracted from the french fries were also determined in duplicate on samples from fry no. 3, 9, 18, 24 and 30 of each day of frying for all 3 fat types, as well as the fat extracted from the pre-cooked frozen french fries. The mean values for each fry are shown in Fig. 8. Again, the values appear to reflect the changes taking place in the frying fat, although not as consistently as did the free fatty acid values of the frying fats. The free fatty acid value of the fat in the frozen french fries was 0.96%, reflecting the composition of the fat in which the fries were blanched by the manufacturer. Thus the free fatty acid values of the fats extracted from the fries at the beginning of the 5 day frying period were 0.12 to 0.14%, representing a balance between the higher free fatty acid values of the fries and the lower free fatty acid values of the frying fats. The free fatty acid values for the final fries after 5 days ranged from 0.99 to 1.19%, very similar to the values of 1.11 to 1.26% for the frying fats.

The regression lines and correlation coefficients describing the increase in FFA with hours of frying are shown in the appended manuscript. There were high correlations of free fatty acid values with hours of frying.

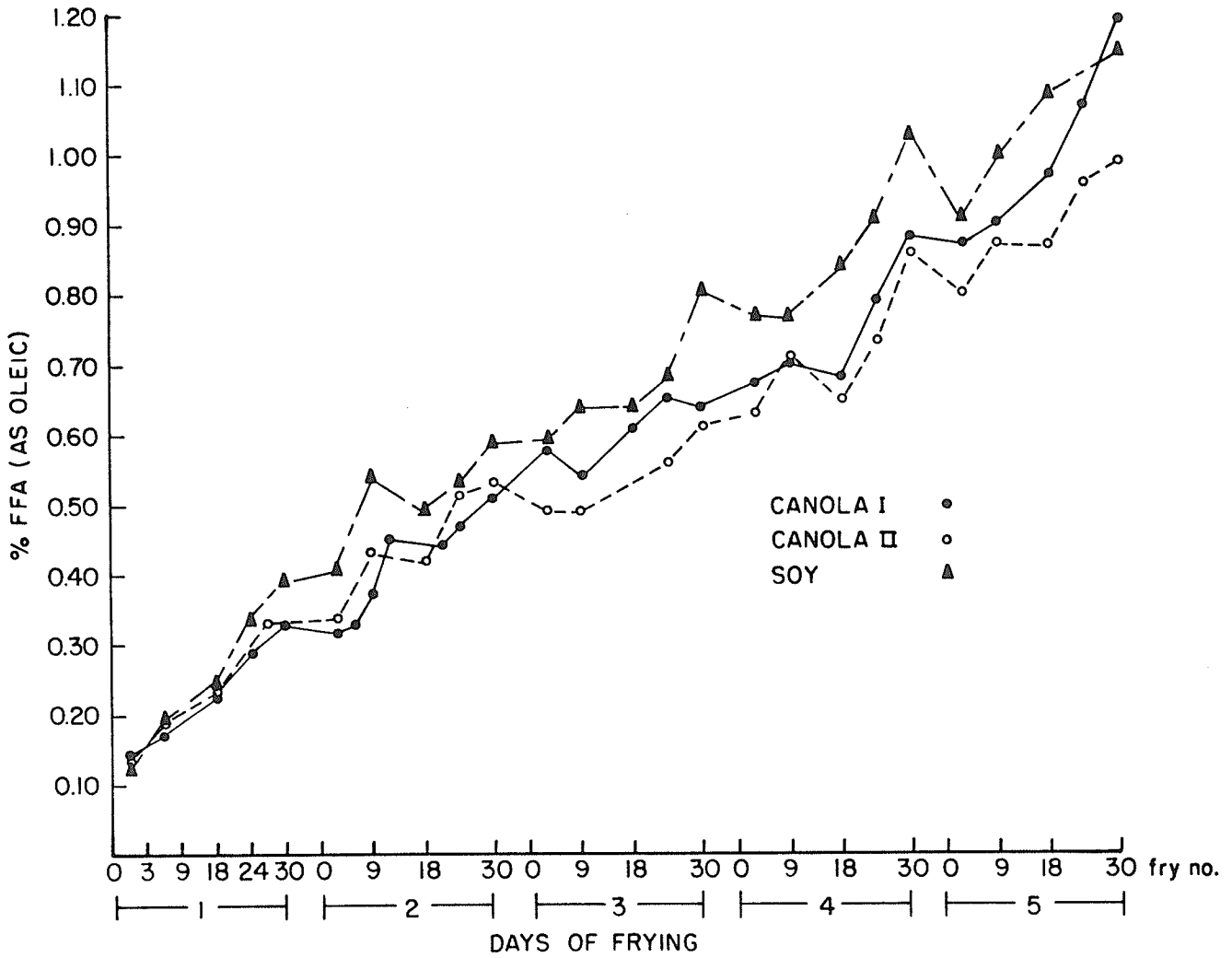

Figure 8: Free fatty acid values of fats extracted from french fries from three types of fats over five days of frying.

B. Polar Components

1. Change in Dielectric Constant

Preliminary testing with the Foodoil Sensor showed erratic results in which the reading for a heated canola fat sample was either 1.0 or negatively off scale on different occasions. The instrument was tested more extensively with a series of 0 to 56 hr used canola fats from a preliminary frying study. The readings taken on four different occasions (replications) are shown in Table 1 along with the FFA values for the fats. There was obviously an increase in deterioration of the fats over the 56 hr of frying as shown by the FFA values which ranged from 0.024 to 1.424%. Although the instrument readings did show a correlation with an increase in hours of frying (Fig. 9), the results were sometime quite variable among the replications. Also, the maximum reading obtained for the 56 hr frying fat was only 1.0 on an instrument scale of 0 to 7 which meant that all readings were in the bottom 15% of the range of scale. As the actual experimental frying fat samples were not expected to fall outside of this 15% of the range, it was concluded that this instrument would not give sufficiently precise readings, and it was not retained for the rest of the study.

TABLE 1: Foodoil Sensor Readings and FFA Values for Hydrogenated Canola Oil Used for Frying French Fries.

Hours of Frying	Instrument Readings Rep 1	Rep 2	Rep 3	Rep 4	Mean ± S.D.	Free Fatty Acids (%)
0	0	0	0	0	0	0.024
8	0	0	0	0	0	0.121
16	0	0.3	0	0	0.08±0.15	0.256
24	0.3	0	0	0.3	0.15±0.17	0.392
32	0.4	0.6	0	0.6	0.40±0.28	0.568
40	0.5	0.5	0.4	0.4	0.45±0.06	0.716
48	0.8	0.9	0.7	0.8	0.80±0.08	1.070
56	1.1	1.1	1.0	0.9	1.03±0.10	1.424

2. Column Chromatography

Although the column chromatography method reported by Billek et al (1978) has successfully been used by other researchers (Paradis and Newar, 1981; Beare-Rogers (personal communication); Waltking and Wessels, 1981), and was considered successful in this study, it was felt that it was too complicated and time-consuming for routine analysis. Therefore, modifications of the procedure were attempted which involved a reconditioning procedure so that the column could be reused. When this proved unsuccessful, the whole column method of Billek et al (1978) was reduced to ¼ scale which offered several benefits. The results of these investigations are detailed in the following sections.

Separation using a 25 g silica gel column. Initially, the method followed was that reported by Billek et al (1978) with the following modifications: (i) the fiberglass wad over the sinctered glass disc was replaced by a disc of fiberglass filter paper which allowed more even packing of the silica gel and retained the fine silica gel particles, (ii) the eluate from the column was collected as individual

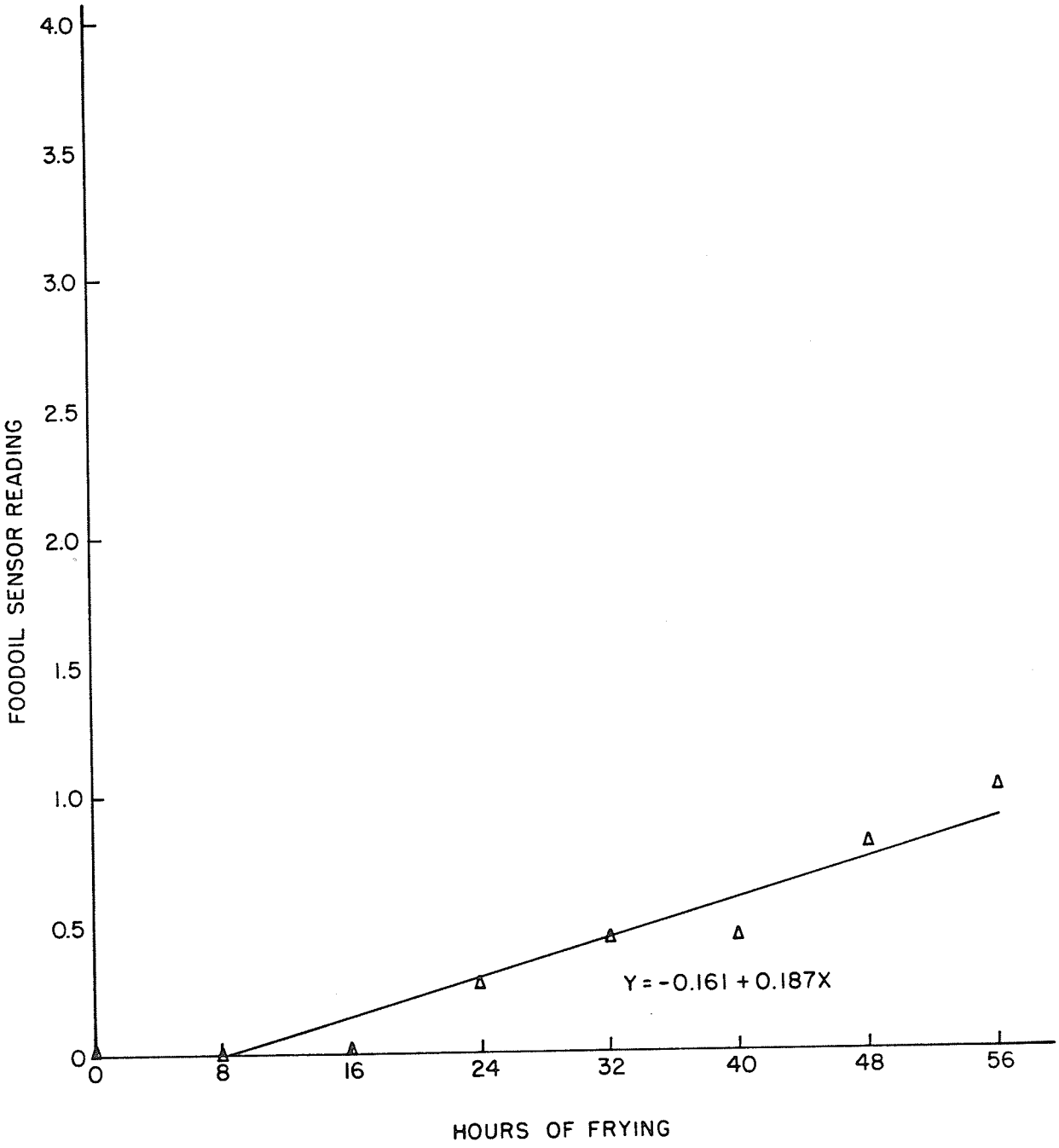

Figure 9: Correlation of Foodoil Sensor instrument readings with hours of frying time.

25 ml fractions rather than two bulk 150 ml fractions and (iii) the exact amount of sample loaded onto the column was estimated by weighing the sample beaker after the second rinsing onto the column. The collection of 25 ml fractions allowed the resolution pattern of the column to be observed, and estimation of the amount of sample loaded onto the column allowed the recovery from the column to be calculated.

Duplicate samples of a 56 hr heated canola fat sample from a preliminary frying study were fractionated on individual columns. A typical chromatogram is shown in Fig. 10. The total fractions (non-polar) eluted with petroleum ether: ether (87:13 v/v) and the total fractions (polar) eluted with ether were each calculated as percentages of the total amount of sample loaded onto the column. The combined non-polar (triglyceride) and polar fractions were calculated as a percentage of the total amount of sample loaded onto the column to determine the recovery. The values for duplicate samples (Table 2) indicated a high degree of reproducibility.

A further 3 samples of a fat from the frying study (code 1-1-0-1) were separated on identically prepared columns in order to estimate the variability of the method. Results are shown in Table 2.

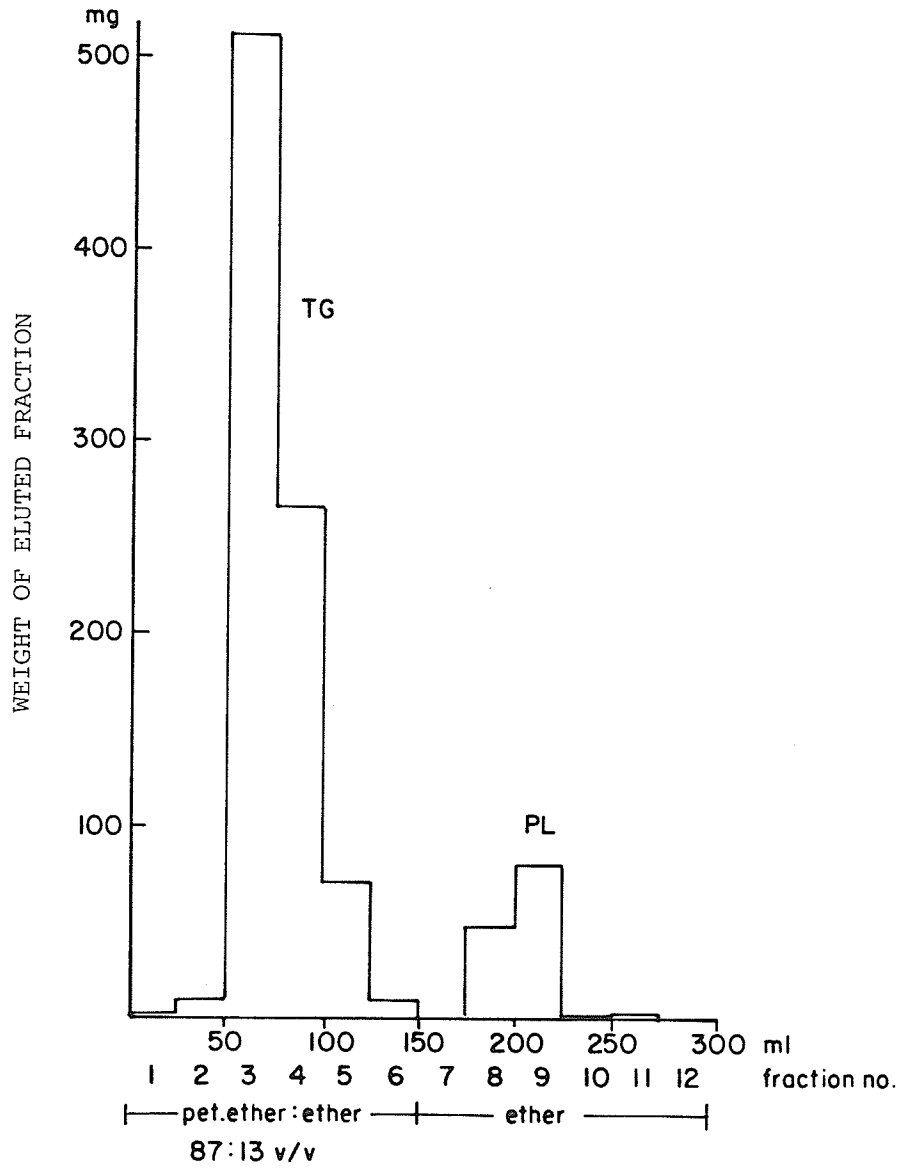

Figure 10: Column chromatography of 1 g of 56 hr frying fat on 25 g silica gel. TG, triglyceride; PL, polar lipid.

TABLE 2: Precision of Replicate Frying Fat Separations on 25 g Silica Gel Columns.

Sample Code	Triglyceride Fraction (%)	Polar Fraction (%)	Recovery (%)
56 hr frying fat	87.26	13.81	101.07
"	86.71	12.17	99.88
Mean	86.99	12.99	100.48
1-1-0-1	95.32	4.60	99.92
"	94.48	6.11	100.59
"	94.02	4.79	98.81
Mean	94.61	5.17	99.77
SD	0.66	0.82	0.90
CV(%)	0.70	15.86	0.90

The standard deviations for the triglyceride and polar fractions, although more than adequate for the purpose of the study, were higher than the standard deviations of 0.3 reported by Billek et al (1978). The initial problems in maintaining an even packing of the column without bubbles may have been affecting the precision in separation of fat on the column.

The method proved to be time-consuming, however, and expensive in terms of column packing and solvents, and thus it would not appear to be the best method for routine analysis of used frying fats. Paradis and Newar (1981) found the column chromatography method to require about 4 hr for each separation. The amount of time estimated for each separation in this study was about 4-5 hr per sample.

Attempted reconditioning of the column between samples. A possible alternative to reduce the time and material cost would be a column which could be reused. Following recommendations by Carroll

and Serdarevich (1967) an attempt was made to wash and regenerate the column between samples, rather than packing a new column.

A sample of 56 hr. frying fat was separated on a new 25 g silica gel column. Following this, the column was washed with 60 ml of petroleum ether: ether (87:13 v/v). A second sample of the same fat was separated on the same column. Although the percentages of triglyceride and polar fractions were similar to those obtained from the new column (Table 3), observation of the elution patterns showed poorer resolution from the washed column (Figure 11, ii).

TABLE 3: Comparison of Chromatographic Separations of a 56 hr. Frying fat on a (i) New and (ii, iii) Reconditioned 25 g Silica Gel Column

Column Treatment	Triglyceride Fraction (%)	Polar Fraction (%)	Recovery %
(i) New Column	87.26	13.81	101.07
(ii) Washed with petroleum ether: ether	84.61	13.90	98.51
(iii) Washed with a series of solvents	82.77	15.02	97.79

A more thorough regeneration using a series of solvents was done on the same column. A third sample of fat on this column showed much poorer resolution with incomplete separation of the triglyceride and polar fractions (Fig. 11, iii), as indicated by the large amount of material in fractions 6 and 7.

In conclusion, as the regeneration procedure adversely affected

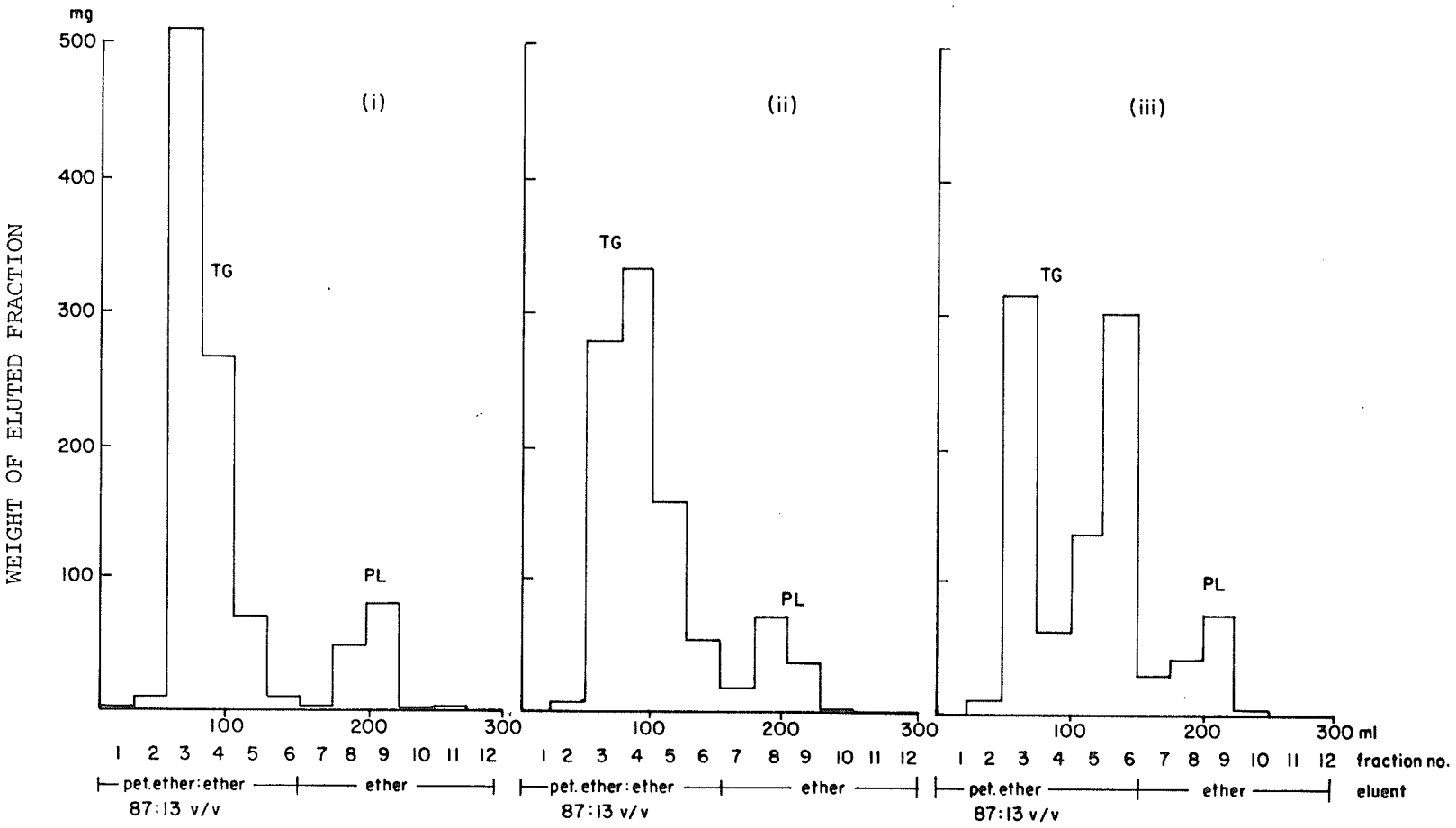

Figure 11: Column Chromatography of 1 g of 56 hr frying fat on 25 g silica gel before and after column reconditioning: (i) separation on a new 25 g column, (ii) second separation, after washing with pet. ether: ether (iii) third separation, after washing with a series of solvents (pet. ether: ether; methanol; acetone; pet. ether: ether). TG, triglyceride; PL, polar lipid.

the resolution on the column, it did not appear to be a feasible alternative.

Separation using a 6.25 g silica gel column. A third alternative, which proved successful, was to reduce the size of the column to ¼ size, thus reducing the time required to pack and run the column and the costs for column packing and solvents. In addition, the smaller column had a higher length/width ratio (25/1.0) than the large column (30/2.1) which should give a better separation efficiency of the fractions (Snyder, 1962).

The procedure for packing and running the column was the same as that for the large column except for the addition of a circulating cold water jacket to the small column which eliminated the bubbles and greatly improved the flow rate.

Triplicate samples of a frying fat (code 1-1-0-1) were separated on individual 6.25 g columns to determine the pattern of resolution and to estimate the variability of the small column method. The results are shown in Table 4.

TABLE 4: Precision of Replicate Frying Fat Separations on 6.25 g Silica Gel Columns.

Sample Code	Triglyceride Fraction (%)	Polar Fraction (%)	Recovery (%)
1-1-0-1	96.26	4.55	100.81
	95.23	4.22	99.45
	96.45	5.13	101.58
Mean	95.98	4.63	100.61
SD	0.66	0.46	1.08
CV(%)	0.69	9.94	1.07

The standard deviations for the triglyceride and polar fractions were 0.66 and 0.46, respectively, as compared to 0.66 and 0.82 (cf. Table 2) for the 25 g column. There appeared to be a better separation of the triglyceride and polar fractions on the 6.25 g column as indicated by the negligible amount of residue in fraction 6 (Fig. 12). On the 25 g column, the triglyceride and polar fractions appeared to overlap slightly in fraction 7 (Fig. 10, p. 52).

A t-test was used to compare the difference between mean values for the large and small columns for the triglyceride and polar fractions. There were no significant differences ($p < 0.05$) between the mean values obtained from the large and small columns.

In conclusion, the 6.25 g silica gel column was found to give results comparable to those from a 25 g column. Considering the savings in time, 40 min as compared to 120 min to run each column, the savings in silica gel, 6.25 g as compared to 25 g per column, and the savings in solvent, 100 ml as compared to 300 ml per separation, this was judged to be a better method for column chromatography of frying fats.

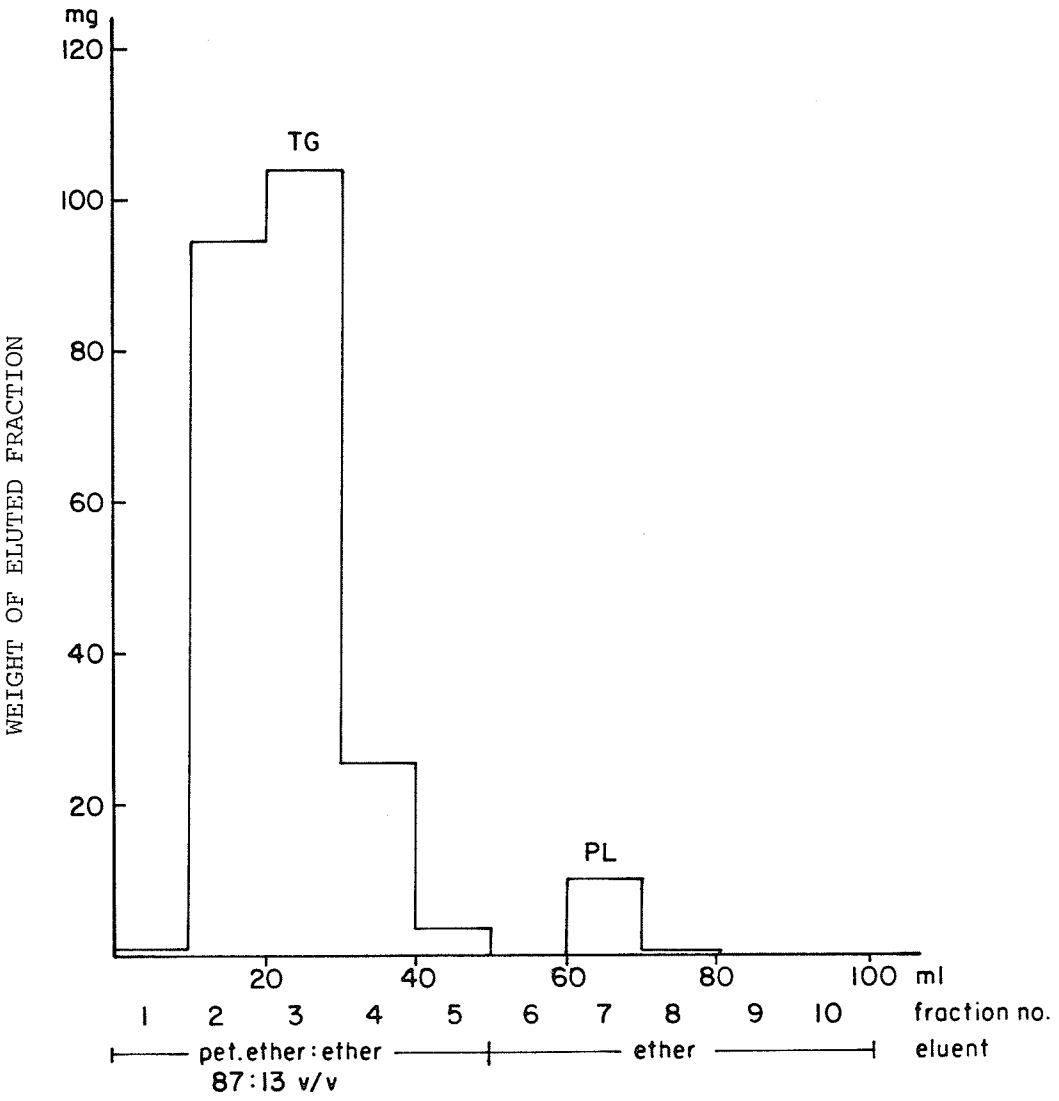

Figure 12: Column chromatography of 250 mg of 56 hr frying fat on 6.25 g silica gel. TG, triglyceride; PL, polar lipid.

Analysis of frying fats. Samples of the unheated fats, and the heated fats from the 30th fry of each day, for each of the 3 fats were chromatographed to determine the percentages of triglyceride and polar components. Results are presented in Table 5. There was an increase in the percentages of polar components in all 3 fats over the 5 days of frying. There was 3.67 to 5.50% of polar material in the unheated fats and this increased to 12.69 to 13.10% after 5 days of frying. These values for the heated fats are much less than the limit of 30% polar material mentioned by Billek (1979) as indicative of severe deterioration in used frying fats, indicating that the length of time or the conditions of frying in this study did not produce severe deterioration in the frying fats. Although no formal sensory evaluation of the french fries was done during this study, comments by the operators indicated that the quality of the frying fat and of the french fries was quite acceptable at the end of the 5 day period. There did not appear to be any distinct differences in contents of polar components among the 3 brands of frying fat used in this study.

These data were combined with additional data from the Department of Foods and Nutrition, using the same method for additional fat samples, and were used to estimate regression lines describing the increases in polar components with increase in hours of frying. The results are detailed in the appended manuscript, but in brief, there were high correlations of percentages of polar components with hours of frying for all 3 fats.

In summary, the determination of polar components by column chromatography appears to be a sensitive and precise method for

TABLE 5: Percentages of Triglyceride and Polar Components in Three Heated Fats from Five Days of Frying.

Sample Code *	Triglyceride Fraction (%)	Polar Fraction (%)	Recovery (%)
1-1-0-1	95.98	4.63	100.61
1-1-24-1	93.78	6.62	100.40
1-2-30-1	90.84	8.80	99.64
1-3-30-1	90.48	9.96	100.44
1-4-30-1	88.11	11.85	99.96
1-5-30-1	87.75	13.10	100.85
2-1-0-1	94.70	5.50	100.19
2-1-30-1	93.79	6.54	100.33
2-2-30-1	92.07	8.26	100.33
2-3-30-1	90.32	9.83	100.15
2-4-30-1	88.99	11.32	100.31
2-5-30-1	87.43	13.02	100.44
3-1-0-1	97.00	3.67	100.20
3-1-30-1	94.53	6.10	100.63
3-2-30-1	92.25	7.57	99.81
3-3-30-1	90.27	10.04	100.31
3-4-30-1	89.64	10.40	100.04
3-5-30-1	87.28	12.67	99.97

* 1,2 or 3 = type of fat; 1-5 = day of frying; 0-30 = fry no.; 1 = frying fat.

monitoring deterioration in frying fats. The use of a ¼ size column reduces the time and materials cost of the method by ¼ and 3/4, respectively. However, it is still a time-consuming method which requires a skilled technician and thus would not be useful as a quick quality control test in the food industry.

3. Thin-Layer Chromatography with Flame Ionization Detection

There were no established procedures to follow for using the Iatroscan system for determination of polar lipids in used frying fats. Thus it was necessary to develop a method which is described in detail in the following section. The percentages of polar components in frying fats determined by TLC-FID using the Iatroscan system were compared to percentages of polar components determined by column chromatography.

Operating variables of the Iatroscan Analyzer. As there appeared to be little concensus as to which hydrogen flow rates corresponded to the various hydrogen pressure settings on the instrument gage, these were checked over the range commonly used on the instrument. The results are shown in Fig. 13. The flow rate of 160 ml/min recommended by the manufacturer corresponds to a gage setting of 0.8 kg/cm^2 - not 1.2 kg/cm^2 as suggested by the manufacturer. Thus, it would appear to be important to check the correlation between flow rate and pressure setting for the particular instrument used.

Initially, the effect of hydrogen pressure on detector response was checked at 1.2 and 1.4 kg/cm^2 for a standard triglyceride sample of 6 µg, spotted on the rods but not developed. The mean peak areas were 18.97 ± 0.97 and 18.94 ± 1.85, respectively, at a scanning speed of 0.31 cm/sec (40 sec/rod). A t-test was used to determine that there was no significant difference between the mean values ($p<0.05$) at the two hydrogen pressure settings. However, a visual appraisal of the scanning at a hydrogen pressure of 1.4 kg/cm^2 revealed that the rods were overheated, which according to Ackman (1981) may shorten

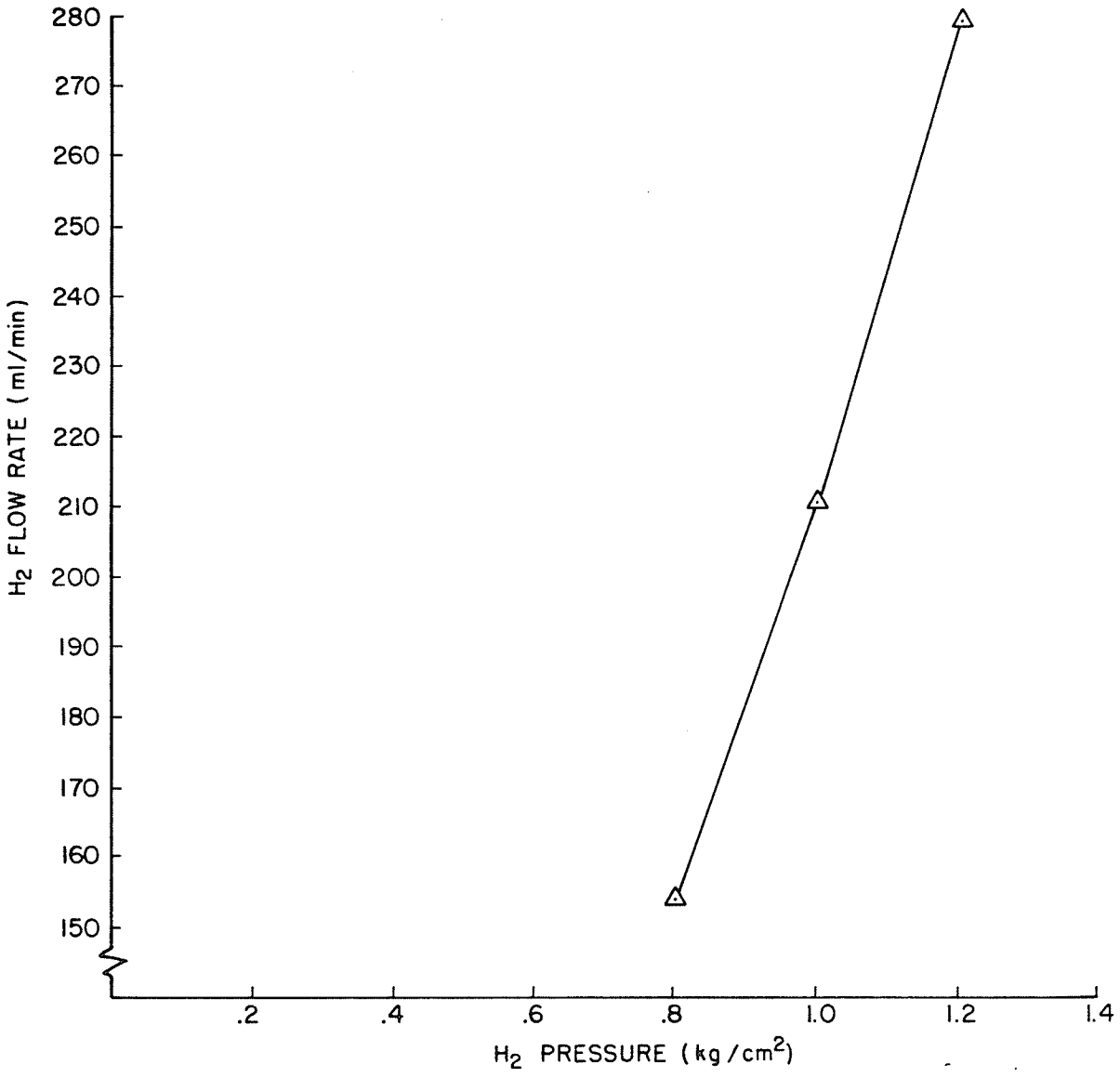

Figure 13: Relationship between H_2 pressure gage setting and H_2 flow rate for the Iatroscan Analyzer.

the life of the chromarods. Also, at the higher hydrogen pressure, the variability of the response was greater, (9.79% C.V.) than at the lower hydrogen pressure (5.09% C.V.).

The effect of hydrogen pressure on response was determined for samples which had first been developed. The scanning speed was increased to 0.41 cm/sec (30 sec/rod). Amounts of 20 µg in 2 µl of solution were spotted, developed and scanned at H_2 pressures of 1.0, 1.2 and 1.4 kg/cm^2. The mean responses for 9 rods at each H_2 pressure are shown in Table 6.

TABLE 6: Effect of Hydrogen Pressure on FID Response* at a Scanning Speed of 0.41 cm/sec.

	H_2 Pressure (kg/cm^2)		
	1.0	1.2	1.4
Mean response	36.93_a	38.24_{ab}	40.96_b
Coeff. of var. (%)	25.16	17.99	15.01

* Values bearing different subscripts are significantly different; $p < 0.05$

An analysis of variance of the data revealed significant differences between mean values at different H_2 pressures (Table 7). Duncan's multiple range test revealed a significant difference between the mean value for 1.4 kg/cm^2 and the value for 1.0 kg/cm^2, but not between the values for 1.0 and 1.2 kg/cm^2 or between the values for 1.2 and 1.4 kg/cm^2.

TABLE 7: Analysis of Variance of Detector Response at H_2 pressures of 1.0, 1.2 and 1.4 kg/cm^2 (Scanning speed, 0.41 cm/sec).

Source of Variation	df	MS	F
Pressure	2	38.007	5.29*
Rods	8	157.021	21.86*
Error	16	7.182	
Total	26		

* $p < 0.05$

Since it was again observed that the rods were overheated at the 1.4 kg/cm^2 pressure, and also that the baselines of the scans were very unstable with excessive background noise, a lower H_2 pressure setting was selected.

At the faster scanning speed of 0.41 cm/sec (30 sec/rod) a hydrogen pressure of 1.2 kg/cm^2 gave a response with a lower variability than a pressure of 1.0 kg/cm^2. However, at a slower scanning speed of 0.31 cm/sec (30 sec/rod) the lower pressure of 1.0 kg/cm^2 was selected to minimize overheating of the rods.

The effect of scanning speed on detector response was checked at two scanning speeds, 0.31 cm/sec and 0.41 cm/sec at a hydrogen pressure of 1.0 kg/cm^2. The mean response at the two scanning speeds were compared by a t-test which indicated no significant difference between the two response values (Table 8).

These results are not in agreement with those of Bradley et al (1979) who reported a greater response and smaller coefficient of variation at faster scannings speeds.

TABLE 8: Mean Peak Areas* (n = 9) for 20 µg Samples Developed and Scanned at Two Scanning Speeds (H_2 pressure = 1.0 kg/cm^2).

	Scanning Speed	
	0.31 cm/sec	0.41 cm/sec
Mean	38.11_a	37.05_a
S.D.	3.68	9.14
Coeff. of Var. (%)	9.66	24.68

* Values bearing different subscripts are significantly different; $p < 0.05$.

It was finally decided to standardize upon a scanning speed of 0.31 cm/sec (40 sec/rod) and a hydrogen pressure of 1.0 kg/cm^2 (flow rate = 210 ml/min) throughout the following study.

Determination of linearity of response and relative response. The response of the detector to weights of lipid ranging from 1-30 µg was determined for both a triglyceride and a polar fraction.

The mean values of integrated peak areas from 9 rods were plotted against weights of the fractions spotted and developed on the rods (Fig. 14). There appeared to be a linear relationship between the weights of material spotted and the peak areas which is in agreement with the findings of Mills et al (1979). A linear regression line was estimated for each fraction using the method of least squares. A lack of fit test was used to test whether the linear regression model was appropriate for the data (Neter and Wasserman, 1974).

The analysis of variance table for the lack of fit test for the polar component data is shown in Table 9.

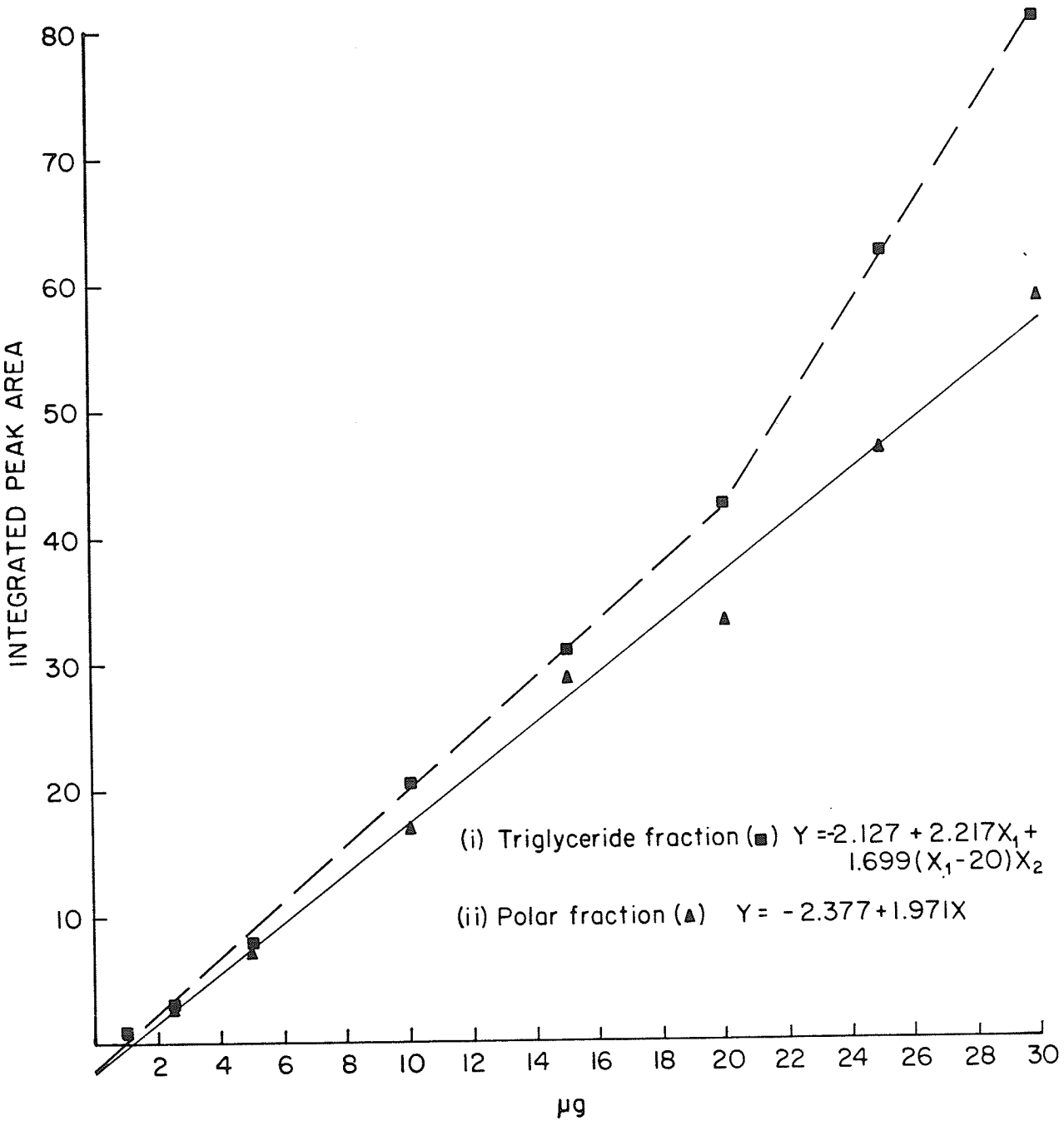

Figure 14: Regression lines and equations describing the relationships between weights of (i) triglyceride fraction and (ii) polar fraction and peak areas. H_2= 1.0 kg/cm^2; scanning speed = 0.31 cm/sec.

TABLE 9: ANOVA Table for Lack of Fit Test for Polar Fraction Data.

Source of variation	df	SS	MS	F*
Regression	1	28,352.099		
Residual	70	2,098.136		
Pure Error	64	1,840.497	28.758	
Lack of Fit	6	257.639	42.940	1.493
Total	71	30,450.145		

The test statistic for the lack of fit test is given by the following equation:

$$F^* = \frac{MS \text{ (lack of fit)}}{MS \text{ (pure error)}}$$

The calculated F* value was 1.493 which was compared to the tabulated F (.95; 6, 64) of 2.35. Since F* < F tab the conclusion was that the linear regression model was appropriate for the data. The equation for the linear regression line for the polar fraction is as follows:

$$\hat{y} = -2.3769 + 1.9712\ x$$

A regression line was estimated for the triglyceride fraction in the same way using the method of least squares. The analysis of variance table for the lack of fit test is shown in Table 10.

TABLE 10: ANOVA Table for Lack of Fit Test for Triglyceride Fraction Data.

Source of variation	df	SS	MS	F*
Regression	1	52,727.396		
Residual	70	2,981.328		
Pure Error	64	2,115.435	33.054	
Lack of Fit	6	865.893	144.316	4.366
Total	71	55,708.724		

The calculated F* value was 4.366 which was compared to the tabulated F (.95; 6, 64) of 2.35. Since F* > F tab., the conclusion was that the linear regression model was not appropriate for the triglyceride fraction data. However, as the data appeared to follow a linear relationship for weights of triglyceride from 1 to 20 µg, it appeared that a piecewise regression model might fit the data. A computer program, using an SAS package, was used to estimate the new regression line. The estimate of the regression line was found to be

$$\hat{y} = -2.2744 + 2.4822x_1 + 1.6099\ (x_1-20)x_2$$

where $x_2=0$ if $x_1 \leq 20$ and $x_2=1$ if $x_1 > 20$. Since the amount of material selected for spotting and developing was 20 µg, $x_2=0$, and the equation $x_1 = \frac{\hat{y} + 2.2744}{2.4822}$ could be used for estimating the equivalent weight (x) of triglyceride from the peak area ($\hat{y}$).

The regression lines and their equations for the triglyceride and polar fractions are shown in Figure 14.

It can also be seen from the regression lines that the mean detector response for the triglyceride fraction was always slightly greater than the mean detector response for the same weight of polar fraction. In order to determine if there were significant differences between the two regression lines, the slopes and intercepts of the two regression lines were tested and found to be significantly different ($p < 0.05$). Thus, there was a significantly greater detector response for the triglycerides than for the polar lipids for the same weight of material. Therefore, it was necessary to use the two regression lines to estimate the weights of triglyceride and polar fractions in unknown samples, and to compare the ratios of weights rather than peak areas.

Although no suitable polar lipid standard could be obtained, it was decided to determine the detector response for a pure triglyceride standard, triolein. Amounts of triolein ranging from 1 to 30 µg were spotted, developed and scanned. The mean peak areas for each weight of standard are shown in Fig. 15. The mean peak areas for the developed triglyceride fraction, isolated from used frying fat by column chromatography (cf. Fig. 14) are shown again in this figure for comparison. As expected, the responses were very similar for triolein and the isolated triglyceride fraction, indicating that the triglyceride fraction isolated from the column was a suitable triglyceride standard for the frying fats. A visual observation of the chromatograms from the triolein and triglyceride standards showed that the positions and shapes of the two peaks coincided, further indicating the similarity of the two standards. Also shown in Fig. 15 is the detector response for triolein which was spotted and scanned but not developed. For all weights of the standard, the detector response was considerably higher for the undeveloped than for the developed standard. Although this phenomenon has not been reported by other researchers, it is in agreement with the observations of Mills et al (1979) that material is progressively "lost" as it migrates up the rods.

A lack of fit test was used to test whether a linear regression model was appropriate for the developed triolein standard data. The analysis of variance table for the lack of fit test for the developed triolein data is shown in Table 11.

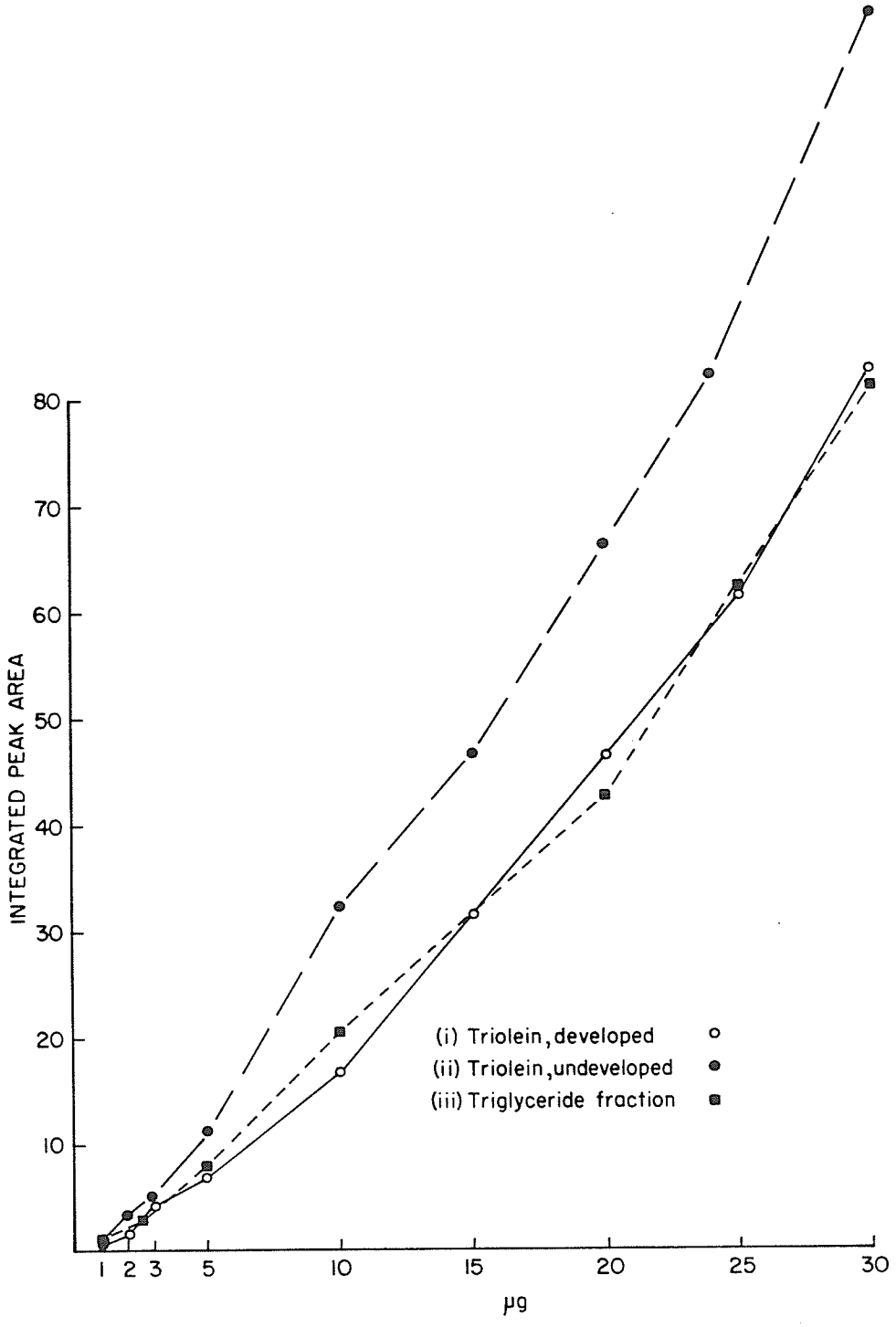

Figure 15: Relationship between weights of (i) triolein, developed, (ii) triolein, undeveloped and (iii) triglyceride fraction, developed and peak areas. H_2 = 1.0 kg/cm^2; scanning speed = 0.31 cm/sec.

TABLE 11: ANOVA Table for Lack of Fit Test for Developed Triolein Data

Source of Variation	df	SS	MS	F*
Regression	1	62,126.255		
Residuals	78	2,120.332		
Pure Error	71	1,152.244	16.229	
Lack of Fit	7	968.088	138.298	8.552
Total	79	64,246.587		

As the calculated F* value of 8.552 was much larger than the tabular F (.95; 7, 71) of 2.17, the conclusion was that the response to increasing amounts of the triolein standard was not linear. Although a regression model was not fitted to the triolein data, it appeared that perhaps a curvilinear relationship might better fit these data. However, it would be preferable to repeat these results and also to determine the response for amounts of standard greater than 30 µg before attempting this analysis.

No attempt was made to fit a regression model to the undeveloped triolein standard data as there would be little interest in quantitating undeveloped standards. However, it would be interesting to determine the response for standards which had been developed to different heights on the chromarods to determine if the response to a given weight of sample is inversely proportional to the height that the sample has migrated up the rod.

Separation of mixtures of non-polar and polar material of known composition. Since the results of separations of the used frying fats by column chromatography had shown that the maximum levels of polar components were in the range of 12-13%, the suitability of the

Iatroscan system for estimating levels of polar components up to 30%, which is considered a maximum allowable level for commercial use (Billek, 1979), could not be determined with the used frying fats. Therefore, a series of mixtures containing amounts of polar components from 4.79 to 34.43% were prepared from the fractions of triglyceride and polar materials eluted by column chromatography. Amounts of 20 µg in a solution of 2 µl were spotted, developed and scanned. Typical chromatograms for mixtures containing 4.79% and 34.43% polar material are shown in Fig. 16.

The mean peak areas for nine rods were calculated for both the triglyceride and polar fractions from each mixture. Using the regression equations for the triglyceride and polar fractions, the corresponding weights of each fraction were estimated from the mean peak areas. The percentage of polar material by weight in each mixture was calculated and is shown in Table 12.

The amount of polar material as determined by TLC-FID corresponded approximately to the known amounts of polar material in the mixtures. The estimation of polar material, 7.26%, was higher than the amount of 4.79% known to be in the mixture, while at the other end at a known level of 34.43% polar material, the estimation of 30.47% was slightly low. A possible explanation for the deviations from the expected results is the large amount of error (C.V. = 22.07 - 52.62%) involved in quantitating the polar peaks, especially at very low levels of polar material. This could possibly be reduced by spotting larger amounts of sample, perhaps 20-40 µg, so that even at very low levels of polar material, the actual weight of material

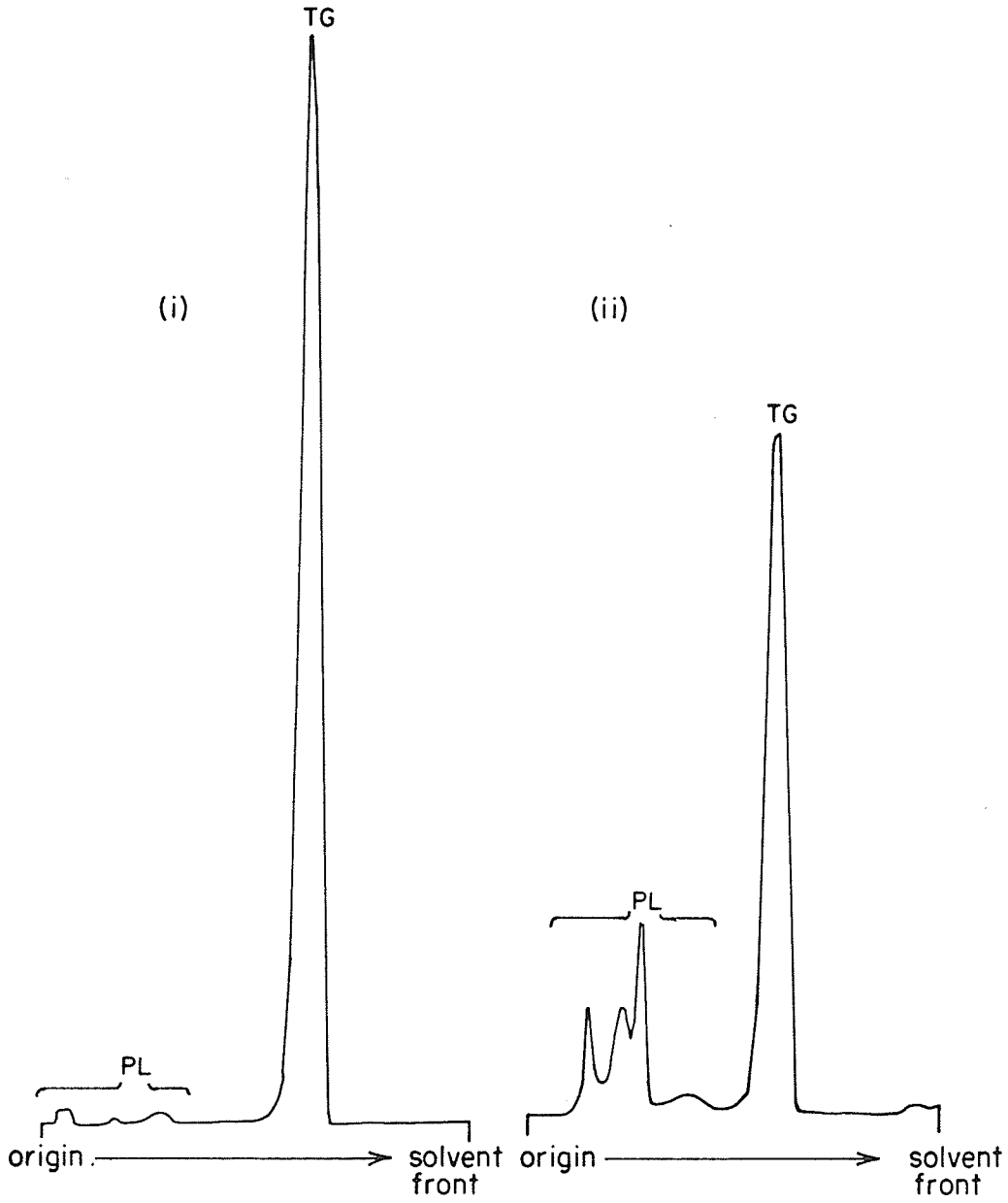

Figure 16: Typical chromatograms of lipid mixtures containing (i) 4.79% polar components and (ii) 34.43% polar components, developed and scanned on chromarods. Sample size = 20 µg; H_2 = 1.0 kg/cm^2; scanning speed = 0.31 cm/sec. TG, triglyceride; PL, polar lipid.

TABLE 12: Mean Peak Areas and Corresponding Weights of Triglyceride (TG) and Polar (PL) Fractions Estimated by TLC-FID from Mixtures of Known Composition.

Known Composition of Mixture	Mean Peak Areas C.V. (%)		Corresponding Weights Estimated from Regression Lines			Estimated Composition of Mixture by TLC-FID
Polar Fraction (% by wt)	TG Fraction (n=9)	PL Fraction (n=9)	TG Fraction (µg)	PL Fraction (µg)	Total TG+PL (µg)	Polar Fraction (Calculated as a % of Total)
4.79	42.91±16.34	0.73±52.62	20.10	1.57	21.67	7.26
9.09	41.46±13.35	1.75±33.23	19.45	2.09	21.54	9.71
14.29	37.53±11.45	2.84±27.65	17.71	2.65	20.36	13.00
20.10	33.44±14.31	3.89±36.79	15.88	3.18	19.06	16.67
24.53	32.29±12.36	5.42±29.71	15.37	3.95	19.33	20.45
29.89	28.35±12.79	7.29±23.65	13.62	4.90	18.52	26.47
34.43	28.54± 6.36	9.57±22.07	13.71	6.06	19.77	30.66

and thus the peak area would be greater.

Analysis of frying fats. Samples of frying fats from the beginning and the end of each frying period for each of the three brands of fats were separated using the Iatroscan system. The percentages of polar material in the fats were calculated from the mean peak areas using the regression equations and are shown in Table 13. For comparison, the percentages of polar material determined by column chromatography (cf. Table 5) are included in the table.

For the unheated fats, the values for polar components by TLC-FID were somewhat high, 6.02 to 7.22%, as compared to values of 3.19 to 5.50% by column chromatography. Conversely, for the fats at the end of the frying period, the values for polar components by TLC-FID were slightly low, 9.93 to 10.77%, as compared to 12.99 to 13.10% by column chromatography. These deviations from the expected results are similar to those observed from the separations from mixtures of known composition.

However, in spite of the variability associated with the Iatroscan Analyzer system, it appears from the above results that the system offers a quick and sensitive method for observing qualitative and quantitative changes in frying fats. Although the initial system is expensive, most of the components are reusable and thus there is little cost involved for materials contrary to the case in the column chromatography methods.

There is room for further development of techniques with the system. The use of different solvent systems and standards might make it possible to quantitatively estimate different classes of compounds

TABLE 13: Mean Peak Areas and Corresponding Weights of Triglyceride (TG) and Polar (PL) Fractions Estimated by TLC-FID from Unheated and Used Frying Fats.

Frying Fat Sample Code	Mean Peak Areas ± C.V. (%)		Corresponding Weights Estimated from Regression Lines			Estimated Composition by TLC-FID	Polar Fraction by Column Chromatography (% by wt)
	TG Fraction (n=9)	PL Fraction (n=9)	TG Fraction (µg)	PL Fraction (µg)	Total TG+PL (µg)	Polar Fraction (Calculated as wt % of Total)	
1-1-0-1	40.42 ± 9.61	0.42±28.53	18.99	1.42	20.41	6.96	4.63
1-5-30-1	38.99 ± 5.19	1.65±18.39	18.35	2.04	20.40	10.02	13.10
2-1-0-1	40.04 ± 9.91	0.54±56.47	18.82	1.48	20.30	7.34	5.50
2-5-30-1	36.40±12.54	1.69±24.73	17.20	2.06	19.27	10.72	13.02
3-1-0-1	42.90±12.75	0.21±32.88	20.09	1.31	21.43	6.13	3.19
3-5-30-1	36.93±10.67	1.81±17.54	17.44	2.12	19.56	10.87	12.99

in the polar fraction. For example, Innis and Clandinin (1981) first separated the polar and non-polar fractions, and then partially scanned the rods which quantitated and removed the non-polar fraction. The rods were then redeveloped in another solvent system which gave a more complete resolution of the polar fraction. This technique could possibly be used with used frying fats to determine the actual amounts of different classes of compounds within the polar fraction.

SUMMARY AND CONCLUSIONS

Canola frying and newer methods for determination of frying fat quality were evaluated in a deep frying study designed to simulate commercial frying operations.

Free fatty acid values were determined by a rapid colorimetric method. The FFA values correlated well with hours of frying for all three types of fat.

Three different techniques for determination of the total polar components in frying fats were evaluated. Changes in dielectric constant were measured by the Foodoil Sensor instrument. The method was neither sensitive nor reproducible and it was felt that the instrument would not provide useful information of the quality of the frying fats.

A reported method for column chromatographic separation of polar and non-polar components gave results of high reproducibility and gave good correlation with increases in hours of frying for all three types of fats. The column chromatographic method was reduced to one-quarter scale which offered considerable savings in time and materials without affecting the accuracy and reproducibility of the results.

A method for the determination of total polar components by TLC-FID using the Iatroscan Analyzer system was developed and evaluated. Results were not as reproducible as those obtained by the column chromatographic method, but the system is rapid and offers a sensitive method of observing qualitative and quantitative changes in

frying fats.

From this study it is difficult to predict which of these methods would be the most useful for monitoring the quality of frying fats. Both the free fatty acid values and the values for polar components as determined by column chromatography correlated well with increases in hours of frying. However, although no formal sensory evaluation was performed in this study, comments by the operators had indicated that the quality of the fat and the french fries was quite acceptable at the end of the five days of frying. The final levels of polar components in the fats, 12-13%, also indicated that only a moderate amount of deterioration had taken place at this time. Therefore, it would be useful in future work to use the fats for a longer period, to the point of discard, and to correlate the analytical values to this endpoint of use.

None of these methods for determination of polar components would appear to be suitable as a routine quality control test for the food industry. The column chromatography method is time-consuming and requires a skilled operator, but has an advantage in that the initial costs for equipment are minimal. The TLC-FID system using the Iatroscan Analyzer is more rapid, but the initial cost of equipment is high, and a skilled operator is required in order to obtain reproducible results. Either of these methods could prove useful in a research or regulatory capacity. However, the challenge still remains to develop a simple and inexpensive method which would be more useful for use in the food industry.

A second goal of this study, which was attained, was to obtain additional information on the behavior of canola frying fats. From

the analyses made in this study, the canola frying fats appeared to perform as well as the soy frying fat. After five days of frying, the levels of free fatty acids were higher in the soy fat than the canola fats while the levels of polar components were similar for both types of fats. Although the conditions and length of frying operation in this study was not sufficient to produce high levels of degradation products, a subsequent study (referred to in the appended manuscript), in which liquid canola and soy frying fats were used for frying for seven day periods, also indicated that the canola fat was as acceptable as the soy fat throughout the frying period.

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APPENDIX

MANUSCRIPT

PERFORMANCE OF CANOLA AND SOYBEAN FATS IN EXTENDED FRYING

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RESEARCH

Performance of Canola and Soybean Fats in Extended Frying

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Abstract

The effects of extended deep frying on chemical and physical changes occurring in hydogenated solid and liquid canola and soybean frying fats were examined in two separate frying studies. Samples of the frying fats and french fries were taken at intervals throughout each experiment and were analyzed for a number of chemical and physical parameters. The values for free fatty acids (FFA) and for polar components (PC) were each highly correlated with hours of frying for all types of fats; therefore, equations for predicting levels of PC from FFA values were calculated. All fats contained only moderate levels of degradation products after 5 or 10 days of frying. These levels of degradation products did not appear to affect the sensory qualities of the french fries adversely, and there were only minor differences in sensory quality between fries cooked in liquid soy or canola fats.

Résumé

Les effets de la friture prolongée sur les changements chimiques et physiques des huiles à frire canola et soja à l'état fluide et à l'état hydrogéné concret firent l'objet de deux études distinctes. Des échantillons d'huiles et de frites furent prélevés à intervalles au cours de chaque expérience et furent analysés pour plusieurs paramètres chimiques et physiques. Les teneurs en acides gras libres (AGL) et en constituants polaires (CP) furent fortement corrélés avec la durée de friture dans le cas de toutes les huiles. On a développé des équations qui permettent de prédire les niveaux de CP et de AGL. Les niveaux de produits de dégradation après 5 ou 10 jours de friture furent modérés dans le cas de toutes les huiles. Ces niveaux de produits de dégradation n'ont pas semblé nuire aux qualités organoleptiques des frites. Les différences en qualité organoleptique furent mineures entre les frites cuites au canola ou au soja.

Introduction

Canola oil, from low erucic acid, low glucosinolate rapeseed, now accounts for more than 40% of the Canadian production of edible fats and oils (Statistics Canada, 1982). Canola oil is processed into a variety of edible oil products including liquid and solid fats for frying. However, to date there have been few publications which describe the performance of canola frying fats in comparison to those which have been commonly used. Such information is needed by existing and potential users of canola frying fats.

Of particular concern is the stability of a fat to the repeated frying carried out in institutional food production. The breakdown products which are formed from fat at frying temperatures include volatile compounds, free fatty acids, cyclic compounds, polymeric triglycerides and other high molecular weight compounds (Chang *et al.*, 1978). These deterioration products in turn cause physical changes such as an increase in viscosity, a darker colour, and a lower smoke point of the fat. As the frying fat is absorbed by the food, thermal oxidation products can be expected to affect its sensory and nutritional characteristics (Holm *et al.*, 1957; Gabriel *et al.*, 1977; Billek, 1979). While many methods have been published to evaluate the changing quality of fat during frying, some sensory judgment of the fried product is often the practical basis for judging when a used fat should be discarded. A more objective test is desirable, particularly one which can be done easily by food service operators and will signal deterioration before nutritional quality is compromised.

Countries such as West Germany and the Netherlands, concerned about the possible nutritional hazards of the thermal oxidation products in frying fats, have specified limits on the amount of deterioration which should be allowed in commercially used fats (Mankel, 1979; van der Heide, 1979). A column chromatographic method for the determination of total polar components (PC) in used fats has been reported to be reasonably reproducible, and while still time-consuming, correlated well with standard tests. For example, a concentration of about 25% PC corresponds to about 0.7% of petroleum ether insoluble oxidized fatty acids, which is one of the West German criteria of fat deterioration (Billek *et al.*, 1978; Guhr and Waibel, 1979; Meyer, 1979).

Many snack food manufacturers and restaurant chains in Canada routinely monitor the percentage of free fatty acids (FFA) in used fat as an indicator of deterioration even though the theoretical basis for so doing is not well defined. Recently Robern and Gray (1981) published a colorimetric spot test which can be used as an indicator of excessive amounts of thermal

oxidation products in fats. While this test essentially depends upon the concentration of FFA, the published results showed that the content of oxidized materials (PC) parallelled the FFA concentration and gross changes produced obvious colour differences (blue to yellow).

The following studies were designed to provide information on a variety of physical and chemical changes which occurred in canola fats during the repeated frying of potatoes under conditions simulating good restaurant practice. Soybean frying fats were studied for comparison. The statistical relationships among the parameters measured were examined to further the development of reliable methods for judging fat deterioration. For the same reason, similar measurements were made, when possible, on the fat extracted from the fried potatoes. While both liquid and solid fats were tested, sensory qualities of fried potatoes were measured only on those fried in the liquid fats.

Materials and Methods

Frozen french fry potatoes (3/8″ regular cut) in institutional pack were obtained from a local wholesale food distributor. The solid fats, two canola and one soybean base, also in institutional pack, were hydrogenated and contained an antifoam agent (dimethylpolysiloxane) and stabilizers. The two liquid fats, one canola and one soybean, were lightly hydrogenated. All fats were obtained directly from the processor.

All frying was done in an institutional electric deep fryer (Garland Model 80-03) which was pretreated with a nonstick lecithin preparation to facilitate subsequent cleaning. Each day the fat was heated to 185 ± 2°C and allowed to equilibrate at this temperature for 15 min prior to frying. One batch (910 g) of potatoes was cooked every 15 min for a total of 30 batches per d (7.5 h). Frying time for each batch was 3 min, followed by draining for 2 min over the fryer. The volume of fat was replenished twice daily with fresh fat after the fifteenth and thirtieth fry. At the end of each day the fryer was turned off and the fat was left in the fryer ovenight to cool to room temperature. Frying was continued for 5 d with the solid fats and for 10 d with the liquid fats for a total of 37.5 h and 75 h of frying, respectively.

Samples of french fries (450 g) and of frying fats (150 mL) were taken at evenly spaced intervals throughout each day. All samples were cooled, flushed with nitrogen and frozen for subsequent chemical and/or physical analyses.

The french fry samples were freeze-dried for 48 h in a Virtis freeze dryer and the percentage of moisture was estimated by the difference in weight. The fat was then extracted from the dried samples by the method of Bligh and Dyer (1959) and the percentage of fat absorbed during frying was determined on a dry weight basis.

Samples of used frying fat and fat extracted from fried potatoes were analyzed in duplicate for the following parameters: thiobarbituric acid (TBA) value (Tarladgis *et al.*, 1962), hydroperoxide value (Eskin and Frenkel, 1976), peroxide value (Cocks and van Rede, 1966), iodine number (AOCS 1979a), FFA (Lowrey and Tinsley, 1976) modified by J. Daun (Grain Reseach Laboratory, Winnipeg, personal communication), fatty acid patterns (Metcalfe *et al.*, 1966) and *trans* fatty acids (Ottenstein *et al.*, 1977). The contents of PC were determined by column chromatography on silica gel (Billek *et al.*, 1978); a new column was used for each sample and the polar fraction was eluted and also weighed.

Physical measurements on the frying fats included the following: measurement of viscosity using a Brookfield viscometer (model C2303 LVT) with the UL sample adaptor at 60°C for the solid fats and at 21°C for the liquid fats, and determination of smoke point following the standard AOCS (1979b) method. Colour changes of the liquid fats were measured using the Hunterlab Colour Difference Meter (Model D25).

Sensory quality of the french fries was evaluated only on those prepared in the liquid frying fat study. This included assessment of exterior crispness, interior dryness, intensity of oil flavour, off-flavours of oil, oily mouthcoat, potato flavour, colour and overall quality. The assessments were done by an eight member trained panel using the line-scale method of Stone *et al.* (1974). The sample of french fries for sensory evaluation was taken from the fourteenth fry on each of days 1, 2, 4, 6, 8 and 10 of the study. Each of these day's sample was compared to a control sample fried in fresh fat just prior to the panel session. All quality parameters except colour were evaluated under red lights in a sensory analysis room with individual booths. Colour was evaluated under natural daylight conditions.

Results and Discussion

The fatty acid composition and *trans* fatty acid content of the unheated solid and liquid frying fats are shown in Table 1 in comparison to those of salad oil. Since essentially no changes were observed in fatty acid composition after extended frying, the values for the heated fats have not been included. The fatty acid compositions of the solid and liquid soybean fats compare favourably with those published by the Consumer and Food Economics Institute (1979). Differences in the composition of Canola I and Canola II solid fats are probably due to variations in processing as they were obtained from different processors.

The content of *trans* fatty acids in processed fats has been reported to vary with both type (selective or non-selective) and the extent (short-time to long-time) of hydrogenation (Teasdale, 1975; El-Shattory *et al.*, 1981). The *ad hoc* Committee on the Composition of Special Margarines has recommended that the Canadian edible oil industry "be encouraged to seek ways to increase the linoleate content while reducing the *trans* fatty acid content of Canadian foods" (Davignon *et al.*, 1980). All solid frying fats contained at least 25% of C18:1 *trans* fatty acids and had a proportion

Table 1. Fatty acid composition of frying fats in comparison to salad oil.[1]

	Solid fats			Liquid fats		Salad oils	
Fatty acid	Canola I	Canola II	Soybean	Canola I	Soybean	Canola	Soybean
14:0	0.3	0.2	0.1	tr	0.1	tr	0.1
16:0	10.2	8.8	12.2	3.8	10.2	4.3	9.3
16:1	—	0.4	tr	0.4	tr	0.3	tr
18:0	13.6	10.1	9.9	2.4	8.0	1.7	3.9
18:1	67.7	73.5	65.0	71.9	43.9	55.2	45.2
18:2	5.3	1.9	11.1	13.7	33.6	26.3	37.2
18:3	0.2	tr	tr	1.2	2.8	9.3	3.2
20:0	0.7	0.7	0.6	1.1	0.6	0.8	0.5
20:1	1.2	1.9	0.4	3.1	0.3	1.7	0.3
22:0	0.2	0.4	0.4	0.3	0.3	0.3	0.2
22:1	0.2	1.4	—	2.0	—	0.2	—
*t*18:1	25.1	44.8	28.8	27.4	9.9	tr	8.7
*c*18:1	42.6	28.7	36.3	44.2	34.0	55.2	36.4
TS+*t*[2]	49.2	65.6	51.6	34.7	28.8	6.3	22.5

[1]g/100 g methyl esters.
[2]Total saturated plus *trans*
(—) — apparently zero

of saturated plus *trans* fatty acids which exceeded the 40% maximum suggested by the Committee (Table 1).

The fatty acid composition of the fat extracted from the uncooked french fries is shown in Table 2. The potatoes were fry-blanched during processing and it would appear, from the presence of traces of erucic acid (C22:1), that canola was the blanching fat. The fats extracted from the french fries cooked in solid fats were almost identical in composition to those of the frying fats (Table 1). These results are in agreement with those of Aust and Thompson (1981), who reported that the lipid composition of partially-fried frozen potatoes reflected that of the finish frying oil. In addition, essentially no change was observed after 5 d (37.5 h) of frying. For these reasons, the fats extracted from the french fries cooked in liquid fats were not analyzed for fatty acid composition.

To estimate the best predictor of change in fats during extended frying, the correlations between hours of frying and the values from physical and chemical tests were estimated and these are shown in Table 3. Of the physical tests, change in colour showed the highest correlation with hours of frying; however, colour changes were measured only in the liquid fats. Smoke points showed the expected negative correlation with hours of frying for all fats. Viscosities gave higher correlations with hours of frying for the liquid fats than for the solid fats, which may be a consequence of the temperature at which viscosities were measured. Of the chemical tests, peroxide values, TBA values, hydroperoxide values and iodine numbers generally showed poor correlations with hours of frying. The highest correlation with hours of frying was shown by the FFA values followed closely by the percentages of PC. Both of these correlations were consistently high among all types of fats.

Table 2. Fatty acid composition of fats extracted from french fries cooked in solid fats.[1]

	Uncooked	Canola I		Canola II		Soybean	
Fatty acid	fries	0 h[2]	37.5 h	0 h	37.5 h	0 h	37.5 h
14:0	0.1	0.3	0.3	0.2	0.2	0.1	0.1
16:0	5.8	9.5	9.1	9.1	8.6	11.0	10.6
16:1	—	—	—	—	—	tr	tr
18:0	7.8	12.3	11.6	9.9	9.8	9.2	9.2
18:1	72.0	69.0	70.2	73.9	74.1	66.8	66.2
18:2	9.6	5.9	5.8	2.1	2.2	10.9	10.8
18:3	0.8	0.4	0.3	—	—	0.2	0.3
20:0	0.9	0.7	0.7	0.7	0.8	0.6	0.7
20:1	1.9	1.3	1.3	1.8	1.9	0.6	1.0
22:0	0.4	0.2	0.3	0.4	0.4	0.3	0.4
22:1	0.7	0.1	0.2	1.4	1.2	—	—
*t*18:1	35.3	26.4	27.1	44.9	42.6	29.3	29.4
*c*18:1	36.7	42.6	43.2	29.0	31.5	37.5	36.8

[1]g/100 g methyl esters
[2]hours used for frying at time of sampling
(—) — apparently zero

Table 3. Correlation[1](r) of hours of frying time with physical and chemical changes in frying fats.[2]

	Physical			Chemical					
Fat	Colour	SP	Viscosity	PV	TBA	HPV	IN	FFA	PC
Solid fats									
Canola I	—	-.80	.76	.34	.54	—	.50	.99	.95
Canola II	—	-.78	.80	.77	.26	—	.28	.99	.97
Soybean	—	-.70	.93	.69	-.31	—	.38	.99	.96
Liquid fats									
Canola I	.97	-.90	.92	.86	.89	.67	-.36	.99	.96
Soybean	.97	-.92	.95	.88	.05	.34	-.19	.98	.96

[1]n = 15 for solid fats; n = 21 for liquid fats.
[2]SP = Smoke point; PV = Peroxide value; TBA = Thiobarbituric acid value; HPV = Hydroperoxide value; IN = Iodine number; FFA = free fatty acids; PC = polar components.
(—) — not analyzed

The values for physical and chemical properties of the frying fats, from the beginning of each study and after extended frying, are shown in Table 4 for the solid fats and in Table 5 for the liquid fats. Within each market form, liquid or solid, the properties of canola and soybean products appeared to be quite similar. The liquid fats darkened with continued heating as would be expected. Solid fats also appeared to darken although actual colour readings were not taken. The smoke point temperatures were initially uniformly low in comparison to the 224°C reported for salad oil (Vaisey-Genser and Eskin, 1982). It should be noted that Arens *et al.* (1977) reported that measurements by the standard AOCS method can vary ± 25°C from one laboratory to another. Smoke points for all fats dropped below 170°C after 15 to 20 h of frying. This temperature has been recommended by the German Society for Fat Research to be used, in conjunction with a concentration of petroleum ether insoluble oxidized fatty acids of 0.7%, as a basis for discarding used frying fat (Billek *et al.*, 1978). Viscosity measurement showed only minor changes in either solid or liquid fats. The FFA and PC values showed distinct increases in all fats as frying time was extended. However, the levels of PC remained well below the 30% which is considered to be indicative of deterioration in used frying fats (Billek, 1979). It is interesting that the contents of FFA and PC in the liquid fats after 37.5 h of frying (Table 5) were no greater than in the solid fats (Table 4). This suggests that the two market forms were equally stable to the frying conditions which were used in this study.

Table 4. Physical and chemical values of solid fats at the beginning and after extended frying.[1]

	Physical			Chemical			
Fat/Time	SP (°C)	Viscosity (Cps)	PV (meq/kq)	TBA	IN	FFA (%)	PC (%)
Canola I							
0 h	208	22.7	0.3	0.034	78	0.03	4.31
37.5 h	152	23.4	4.9	0.058	73	1.16	13.10
Canola II							
0 h	209	23.8	4.4	0.024	76	0.04	4.51
37.5 h	134	24.5	7.8	0.024	76	1.11	13.42
Soybean							
0 h	212	22.3	0.9	0.014	83	0.01	2.51
37.5 h	152	23.2	4.2	0.066	80	1.26	12.70

[1]Definitions as per Table 3

The correlations between hours of frying and physical and chemical values of the fats extracted from the french fries are shown in Table 6. The highest correlations were between FFA values and hours of frying and between percentages of PC and hours of frying, as in the frying fat samples. The percentage of fat absorbed did not correlate well with hours of frying.

The values from all physical and chemical tests on the fats extracted from the french fries are shown in Tables 7 and 8. There were no significant differences in the amounts of fat absorbed from the solid or liquid

Table 5. Physical and chemical values of liquid fats at the beginning, during, and after extended frying.[1]

	Physical			Chemical					
Fat/time	Colour (ΔE)	SP (°C)	Viscosity (cps)	PV (meq/kg)	TBA	HPV	IN	FFA (%)	PC (%)
Canola I									
0 h	21.0	194	21.6	0.8	0.002	0.024	94	0.00	3.41
37.5 h	36.9	144	22.8	1.8	0.060	0.041	96	1.00	11.72
75 h	42.2	121	23.4	2.9	0.058	0.057	91	2.26	15.12
Soybean									
0 h	21.0	218	18.7	1.8	0.096	0.000	97	0.00	4.84
37.5 h	34.0	152	20.4	2.8	0.034	0.041	101	0.60	10.57
75 h	42.6	134	21.2	4.2	0.056	0.026	88	1.73	15.33

[1]Definitions as per Table 3

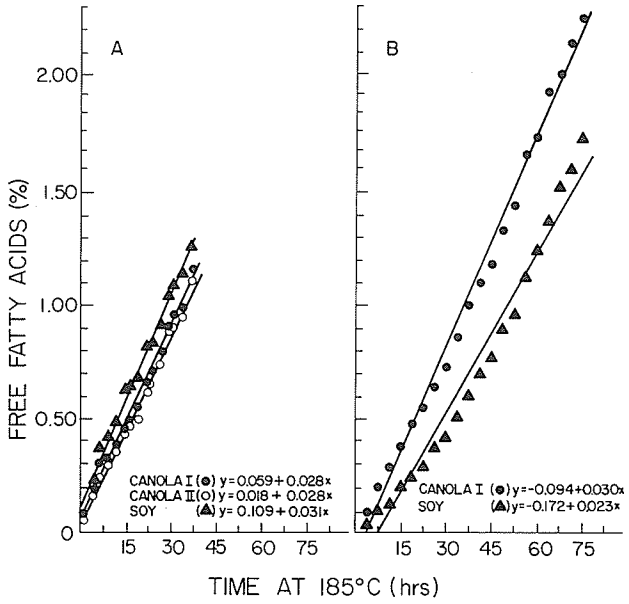

Fig. 1 Relationship between FFA and hours of frying time in: A. Solid frying fats; B. Liquid frying fats.

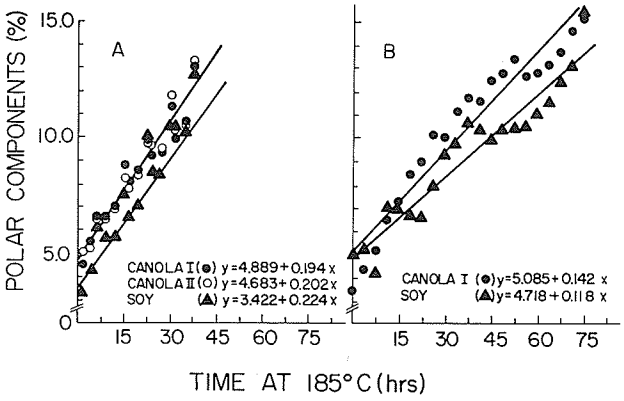

Fig. 2 Relationship between PC and hours of frying time in: A. Solid frying fats; B. liquid frying fats.

forms of soybean or canola fats, although lower values were observed with the use of the liquid soy product. Yang and Chen (1979) suggested that less fat was absorbed when frying in liquid fat than in solid fat. The peroxide values, TBA values, hydroperoxide values and iodine numbers showed little change from the beginning to the end of either frying study. The percentages of FFA and of PC in the fats extracted from fried potatoes appear similar to the values obtained from the frying fats (Tables 4 and 5). However, in the case of the PC values less confidence can be placed in the data from fats extracted from potatoes due to difficulties in recovering all PC from the columns. It was observed that 5-10% of the non-triglyceride fraction remained strongly adsorbed on the column. This difficulty may also be observed in the data reported by Alim and Morton (1974) which suggested that thermal oxidation products were preferentially absorbed by fried foods.

Because of the high correlations that existed between FFA values in used fats and hours of frying time and between percentages of PC and hours of frying times (Table 3), these relationships were plotted and are shown in Figures 1 and 2 respectively. It is obvious that both of these measurements of frying fats could be used as predictors of the changes taking place in the french fries.

Since FFA analysis is a much simpler and faster test to perform, and correlated as well with frying time as did the accumulation of PC, it appears attractive to use only FFA analysis as a measure of deterioration in frying fat as suggested by Robern and Gray (1981). The validity of predicting the accumulation of PC from FFA values was examined by estimating the correlation coefficients between the two sets of data for canola and soybean fats in both the frying fats and the fats extracted from the french fries (Table 9). As expected, the correlations between the contents of PC and FFA were high in all cases ($p > 0.9$). However, significant differences among slopes (b) and/or intercepts (a) of the regression equations prohibited the calculation of a generalized equation. The relationship between FFA and PC formation during frying appeared to vary with the market form of the frying fat (Figure 3). The regression lines for the solid fats uniformly had larger b values than for the liquid fats (Table 9). Thus, a given increment in FFA would correspond to a larger increase in polar components in the solid fats than in the liquid fats. The solid soybean fat initially had the lowest content of PC of any of the five frying fats tested (Tables 4 and 5). Accordingly, in the regression equations (Table 9) the (a) value for the solid soybean fat was low, although the rate of accumulation of PC in response to increases in FFA (b) was similar to that in solid canola fat. The relationships between FFA values and percentages of PC in the fats extracted from the french fries were similar to those of the frying fats but the difference between solid and liquid fats was less distinct.

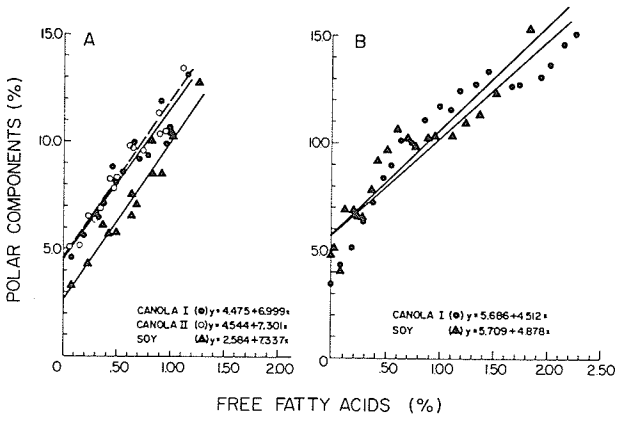

Fig. 3 Relationship between contents of PC and FFA in: A. Used solid frying fats; B. Used liquid frying fats.

Table 6. Correlation[1] (r) of hours of frying time with physical and chemical changes in fats extracted from french fries.[2]

Fat/time	Physical	Chemical					
	Fat absorption	PV	TBA	HPV	IN	FFA	PC
Solid fats							
Canola I	-.04	-.68	.45	.69	.54	.98	.96
Canola II	.12	.59	.74	.46	.15	.99	.95
Soybean	-.14	-.42	.74	.66	-.66	.99	.99
Liquid fats							
Canola I	-.28	.33	.08	.61	-.49	.99	.98
Soybean	-.12	-.39	.19	-.34	-.49	.98	.97

[1]n = 15 for solid fats; n = 21 for liquid fats
[2]Definitions as per Table 3

Table 7. Physical and chemical values of solid fats extracted from french fries cooked at the beginning and after extended frying.[1]

Fat/time	Physical	Chemical					
	Fat absorption (%)	PV	TBA	HPV	IN	FFA (%)	PC (%)
Canola I							
0.75 h	12.4	0.4	0.066	0.067	54	0.14	5.43
37.5 h	10.0	7.5	0.118	0.138	70	1.19	10.78
Canola II							
0.75 h	15.2	2.0	0.006	0.154	73	0.14	4.49
37.5 h	16.6	10.1	0.120	0.340	72	0.99	10.92
Soybean							
0.75 h	13.3	4.7	0.010	0.138	77	0.12	3.53
37.5 h	14.2	3.8	0.058	0.296	68	1.15	10.88

[1]Definitions as per Table 3

Within the solid fats, although the slopes (b) of the FFA:PC relationships were similar for soybean and canola fats, there were significant differences in intercepts (a) which meant that a general equation for solid fats from both oil sources was not valid (Table 9). Within the liquid fats, however, there were no significant differences between either slopes (b) or intercepts (a) so that the combined equation for soybean and canola liquid fats could be estimated; it is shown in Table 9. Although not conclusive, these data comparisons do suggest that the FFA content of frying fats has predictive value for PC. This prediction, however, is based on only two experiments, and requires further validation before it can be generalized for all types of frying fats under varying frying conditions.

The results of the sensory analyses of the cooked french fries from the liquid frying fat study showed that, in general, there were few significant differences in the quality of the french fries from the beginning to the end of the study (Table 10). These findings tend to confirm the results of the chemical tests in which only moderate amounts of deterioration in the frying fats were detected. Within the canola fat series, the french fries on day 1 were judged to have significantly less oily mouthcoat ($p < 0.05$) than the french fries cooked on any other day. Within the soybean fat series, the french fries cooked on days 1 and 2 were judged significantly ($p < 0.05$) less crisp than french fries cooked on all other days. In all other characteristics, within each fat, the french fries were considered similar throughout the 10 day frying study.

In examining the sensory differences between soybean and canola fats, over all days of frying, the french fries cooked in canola fat were judged to be less dry and mealy, less crisp, and lighter in colour than those fried in soybean fat. The "overall" quality scores, which represent a subjective integration of all characteristics, were significantly higher ($p < 0.05$) for the french fries cooked in canola fat. It should also be noted that even after 10 d of frying, the panel found the french fries cooked in either canola or soy liquid fat to be very acceptable despite the fact that the fats contained 1.2 and 2.8% linolenic acid. Holm *et al.* (1957) and Smouse (1979) have reported that the intense reversion flavours in some heated oils may be related to formation of high molecular weight unsatu-

Table 8. Physical and chemical values of liquid fats extracted from french fries cooked at the beginning and after extended frying.[1]

Fat/time	Physical	Chemical					
	Fat absorption (%)	PV	TBA	HPV	IN	FFA (%)	PC (%)
Canola I							
0.25 h	12.1	1.9	0.034	0.074	90	0.03	4.57
37.5 h	14.2	2.5	0.056	0.076	85	0.84	10.09
75 h	10.9	3.7	0.046	0.088	82	1.93	15.50
Soybean							
0.25 h	9.4	6.9	0.022	0.070	97	0.04	3.99
37.5 h	8.7	4.4	0.028	0.096	90	0.56	7.93
75 h	5.4	5.3	0.022	0.096	88	1.60	13.03

[1]Definitions as per Table 3

Table 9. Relationships between free fatty acids and polar components in frying fats and in fats extracted from french fries (where y = a + bx).

Type of fat	r	a	b	Response[1]
Frying fat				
Solid				
Canola I	.96	4.48	6.99	3.49
Canola II	.97	4.54	7.30	3.65
Soybean	.97	2.58	7.34	3.67
Liquid				
Canola I	.93	5.69	4.51	2.27
Soybean	.94	5.71	4.88	2.44
Combined liquid fats	.94	5.76	4.58	2.29
Fat extracted from french fries				
Solid				
Canola I	.95	4.64	5.33	2.66
Canola II	.96	4.30	6.96	3.48
Soybean	.99	2.77	6.85	3.42
Liquid				
Canola I	.98	5.27	5.40	2.70
Soybean	.95	5.16	5.86	2.93

[1]Predicted increase in polar components (y) to a 0.5% increase in free fatty acids(x).

Table 10. Averages scores[1] from sensory evaluation of french fries (liquid frying fat).

Fat/time	Overall quality[2]	Oily mouthcoat	Colour[2]	Exterior crispness[2]	Interior dryness[2]	Potato flavour	Oil flavour intensity
Canola I							
Day 1	1.88	0.40[a]	1.19	0.79	1.77	1.30	0.53
Day 10	1.34	0.88[b]	1.30	1.13	1.42	0.98	0.97
Soybean							
Day 1	1.71	0.39	1.67	1.32[a]	2.76	1.39	0.68
Day 10	1.42	0.54	1.65	1.54[b]	2.87	1.16	0.95

[1]logs of standardized mean panel scores (n = 8); higher value represents more of the characteristic.
[2]denotes significant difference ($p<0.05$) between canola and soy over all days.
[ab]values in the same column for the same fat bearing different letters are significantly different ($p<0.05$).

rated compounds from linolenic acid. As these compounds would be expected to be in the polar fraction of the fat, the content of PC would be expected to relate to the acceptability of the fat. However, it appeared that the levels of PC reached in this study were insufficient to cause a decrease in the acceptability of fried potatoes. From a processing point of view, it would be useful to determine at what level of PC the sensory quality of the fried product begins to be adversely affected; Billek (1979) has suggested that this level is 30%.

In summary, FFA values and contents of polar components gave the best correlations with hours of frying in these studies. Since the correlations between these two tests were high, and since the method for PC is more complex, the determination of FFA may be the best method for monitoring fat deterioration during extended deep frying. Several equations for predicting the contents of polar components from the FFA values for different types of fat are provided. The sensory scores of potatoes, fried in liquid fats showed remarkably few differences due to either oil source or the length of time the fat had been used. After 10 days of use the FFA values of the liquid fats ranged from 1.7 - 2.3% and contents of PC ranged from 13 — 16%, yet the potatoes fried in these fats were judged as acceptable. Further work is required before critical levels of FFA or PC for discarding frying fats can be recommended.

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