
Commercial Assessment of Quality in Frying Oils

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Frying is a universally popular means of cooking. It is carried out in one of three ways:

- (a) In a shallow frying pan — the oil is virtually used up each time.
- (b) In a deep pan — the oil is used for several or many batches of fried food.
- (c) In large scale continuous fryers — the oil is used for prolonged periods.

Operations of types (b) and (c) are the only processes where a food — the frying oil — is heated to a temperature above 100°C for prolonged periods. (Although a baking oven may be operated at 220°C—250°C, it is only a thin layer at the surface of the baked product that gets more than a few degrees above boiling point). Frying is usually carried out at 180°C ± 5°C, and at this temperature the oil undergoes a number of reactions. The processes occurring are shown diagrammatically in *Figure 1*.

Chemical changes occur within the oil itself, and as a result of interaction between the oil and the atmosphere, and between the oil and the food being cooked and its water content.

Many chemical and analytical studies have been made to identify and quantify the reaction products. These studies have had two main objectives: firstly, to establish whether any nutritionally harmful products are formed at a significant level, and secondly, to find analytical criteria, preferably simple ones, which would provide decision points for the discard of oils. Regulatory authorities need to decide whether food products are fit for consumption (Mankel, A., 1979 and Begemann, O., 1986), while manufacturers (most, if not

all) want to maintain a consistent quality and need objective criteria for the discard of an expensive food ingredient.

Various studies of batch (type b) and continuous (type c) frying operations have led to the general conclusion — not unexpected — that the batch process is much more variable and more likely to lead to the use of excessively abused oils, possibly with toxic properties. The batch process is mainly used in restaurants, fast food outlets, fun fairs and street stalls. Temperature control may be poor, demand fluctuates, and the operators may be relatively unskilled, in comparison with those working a continuous process. The batch process therefore provides the greatest challenge to the control chemist.

SELECTIVE REVIEW OF ANALYTICAL METHODS

Sophisticated Tests

Oxidized fatty acids. This is an officially accepted method, in which the fatty acids insoluble in petroleum ether are determined gravimetrically. It is not a very satisfactory method since it does not measure all the oxidized acids, and is difficult to carry out.

Polymeric triglycerides. Polymeric and unchanged glycerides can be separated according to size (molecular weight) by gel permeation chromatography on columns of cross-linked polystyrene (Guhr *et al.*, 1978). The method has the disadvantage that partial glycerides naturally present in an unheated oil are also determined. There is therefore a need for a

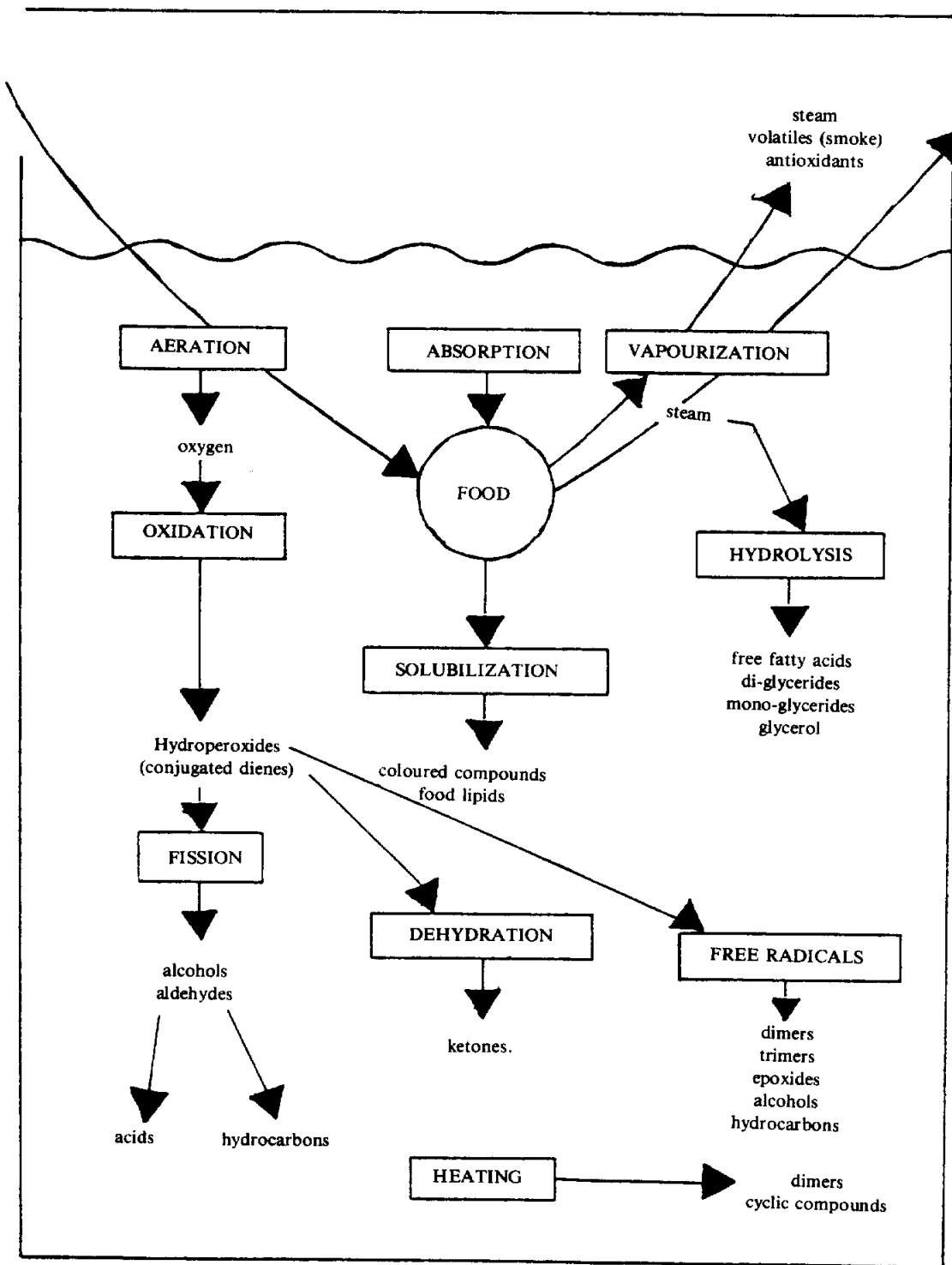


Figure 1. Changes Occuring in Frying Oil.

control determination on the unused oil. Recently the use of SEP-PAK cartridges has been recommended (Sebedio *et al.*, 1986). This gives the same results much more quickly.

Exclusion chromatography on beads of polystyrene divinyl benzene copolymer enables dimers and higher polymers to be determined separately but does not separate oxidized from unchanged triglycerides (Perin *et al.*, 1984). Size exclusion chromatography on Beckman spherogel columns can also be used (White *et al.*, 1986).

Gere (1984) used a more complex scheme. Adsorption chromatography on silica produced a non-polar, a polar and a highly polar fraction. These fractions were then further separated by exclusion chromatography on sephadex LH20 to give quantitative analyses for:

1. Unaltered triglycerides
2. Polymers — non-polar and oxidized together
3. Oxymonomers
4. Diglycerides — unaltered and oxidized
5. Free fatty acids and other low molecular weight polar compounds.

Billek *et al.* (1978) examined a large number of commercially used frying oils by four methods:

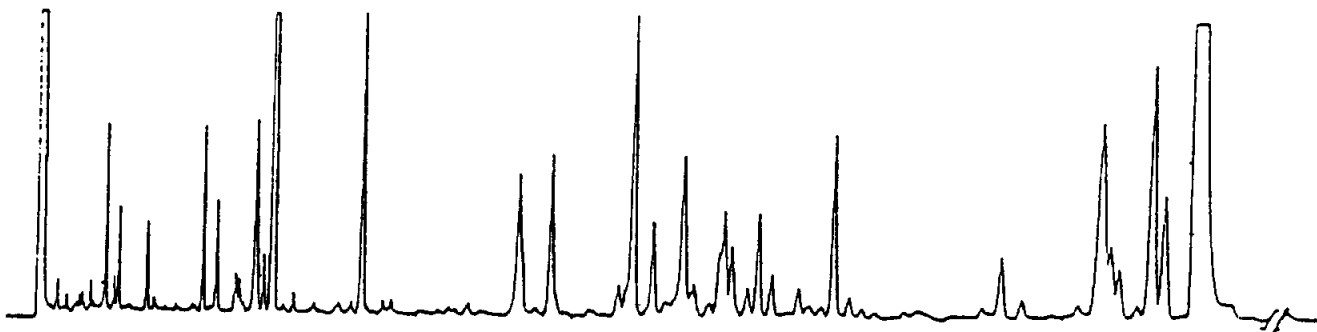
1. Oxidized fatty acids insoluble in petroleum ether.
2. Polymers by Guhr and Waibel's method, described above.
3. Total polar artifacts by liquid chromatography on silica gel. (A moving wire detector was used).
4. Column chromatography to measure unaltered triglycerides (and if desired, polar compounds). Silica gel containing 5% water was used in an adaptation of a procedure first used by Sen Gupta for separating phosphatides from trigly-

cerides. Unaltered glycerides were eluted with petroleum ether:ether (87:13) and weighed.

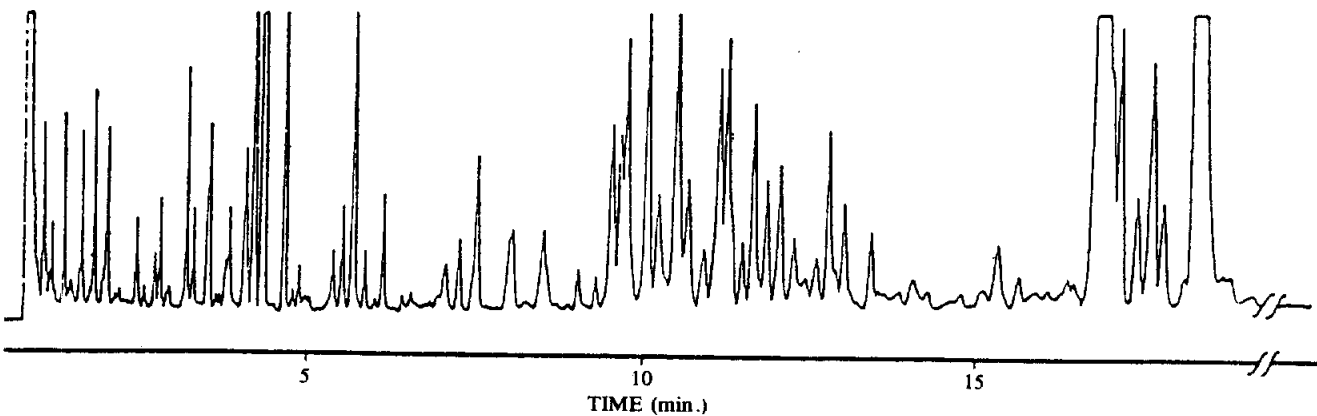
Methods (3) and (4) are similar in principle. Method (4) was the simplest and most reproducible. Method (1) is unsatisfactory because some oxidized fatty acids are soluble in petroleum ether. However, regrettably, it has been adopted by local authorities in West Germany. Method (4) has been tested and adopted by IUPAC and the AOAC (Walking *et al.*, 1981) and successfully used by J. Castang (1981) for the analysis of used frying oil, from restaurants.

Cyclic monomers. These products of the action of heat on unsaturated fatty acids are important because they have been shown to be nutritionally undesirable. Levels as low as 0.15% in the feed cause metabolic disorders in rats (Iwaoka *et al.*, 1976). A major investigation was reported in 1972 by Artman and Smith. They separated a distillable fraction from heated cottonseed oil that did not form an adduct with urea. GLC of the fraction gave 136 peaks, of which 51 were characterized. About 0.14% of the heated oil consisted of cyclic monomers. More recently Frankel *et al.*, (1984) analysed a large number of commercially-used frying oils from the USA and from Middle East outlets. They found 0.1% — 0.5% cyclic monomers in US samples and 0.2% — 0.7% in those from the Middle East. Rojo *et al.* (1987) used gel permeation chromatography on Biobeads SX2 to fractionate used, partly hydrogenated soya bean oil according to molecular size. Individual fractions were converted to methyl esters, hydrogenated, fractionated with urea and analysed for cyclic monomers by capillary GLC. Thirteen specific C18 cyclic monomers were identified by GC-MS. The fresh oil contained a total of 736 ppm of these 13 components, while the heated oil contained 1803 ppm (see *Figure 2.*)

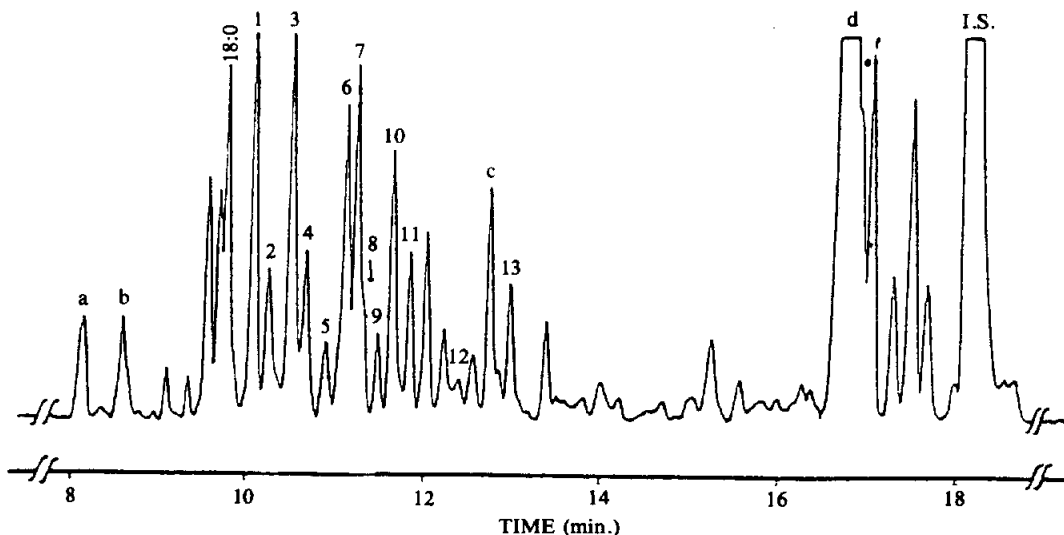
FRESH OIL



HEATED OIL (80 Hr. @ 195°C)



Capillary GLC chromatograms of non-urea adducting (NUA) fractions.



Partial chromatogram of heated oil NUA-fraction showing peak codes used for the study. I.S., Internal standard — Phenanthrene (RRT = 1.845, ECL = 20.324).

Figure 2. Cyclic Monomers in Frying Fats
(from Rojo and Perkins, 1987).
(reproduced with permission from JAOCS)

Measurements of oil stability. Several methods are now widely used, for example the AOM Test, the Swift Test, Rancimat, and the FIRA Astell Oxygen Absorption Test.

These tests are not relevant to frying oils when the products are intended for immediate consumption but they become very important when the products are required to have a shelf life (Berger, 1971). Stringent control of the frying operation is required if the shelf life is to be guaranteed.

Determination of hexanal. The GLC determination of hexanal in the headspace above a convenience food (instant noodles) has been correlated successfully with the development of rancidity during storage, and used to test the effectiveness of antioxidants (Rho *et al.*, 1986). (See *Figure 3*). The figure shows the development of hexanal in stored noodles that had been fried in palm oil with and without the addition of antioxidants.

Simple Analytical Tests

Free fatty acids. As oil is used for frying, the titratable acidity increases both as a result of hydrolysis due to the steam generated and — to a lesser extent — because of the formation of acidic oxidation products. The rate of FFA development depends on the process parameters and the food being fried, and therefore a limit for FFA must be decided for each operation. FFA development runs parallel to other chemical changes.

Mlinar (1986) has reported the development of test strips for FFA measurement. They are made entirely for food grade material and can be safely used in the kitchen. Each test strip is divided into a number of separate 'cells' by stripes of silicone polymer. Each cell is a separate reaction chamber impregnated with an indicator and a different level of reactant. On dipping into the oil, a colour change is observed in some or all of

the cells, depending on the acidity. The strips have been tested at PORIM and they performed well.

Colour. Colour development is readily measured in a Lovibond tintometer or in a spectro-photometer at a chosen wavelength (for example, 363 nm). For use in the kitchen a simple comparator can be used with a standard colour solution to provide a limit test.

The author instituted such a test quite successfully in Lyons teashops in London. The 'rejection' colour was decided by management. Over a period of months it was found that a significant amount of oil was saved because many chefs were discarding oil on a weekly routine whether it had been much used or not.

Smoke point. This is an important practical parameter related to the volatiles present in the oil (including FFA). Excessive smoking is objectionable and presents a fire risk. *Figure 4* shows several results of the relationship between smoke point and free fatty acids. Unfortunately the accepted method (AOCS Method CC9—48, 1979) is not very reproducible, and it may be hoped that the automated method published by Bregulla and Seher (1979, 1980) will eventually be more widely used.

Foam test. Another practically important result of deterioration in a frying oil is the production of a stable foam, which can become a serious fire risk. Various empirical foam test procedures have been described (*e.g.* by Bracco *et al.*, 1981).

Perrin *et al.* (1985) analysed groundnut and sunflower oil when they had developed a stable foam, and concluded that foam stability was due to higher proportions of polar glycerides and particularly the higher polymers. Their results are shown in *Table 1*.

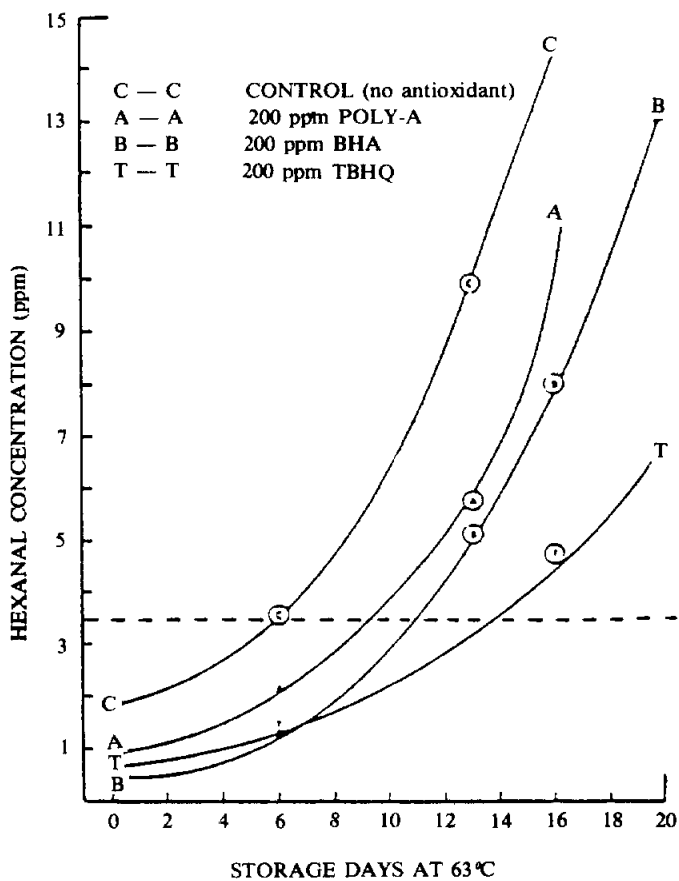


Figure 3. Hexanal concentration vs storage days of ramyon (instant noodles) at 63°C (145°F). The circled points on the curves have a rancid taste as determined organoleptically. The dotted line denotes the concentration of hexanal which can be detected organoleptically in ramyon. The average standard deviation of hexanal in the ramyon was ± 0.54 ppm. (Reproduced with permission from JAOCs).

B — From Bailey
 H-S Soyabean Oil — Hartmann *et al.* (1975)
 H-B Babassu oil — Hartmann *et al.* (1975)
 P — PORIM — Used frying oils

} FFA added to oils

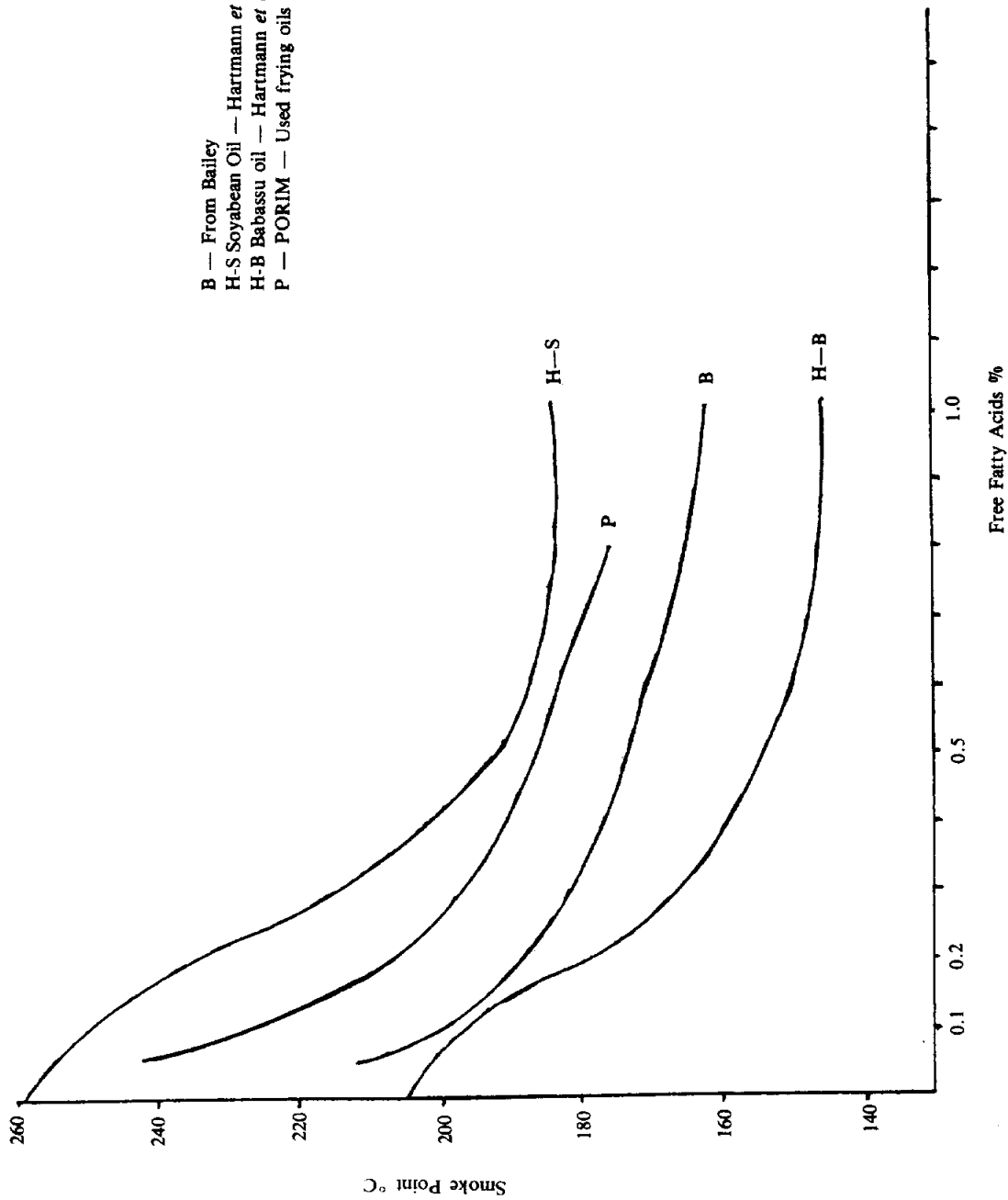


Figure 4. Effect of FFA on Smoke Point

Alkaline Contaminating Material. Blumenthal *et al.* (1985) proposed a quick test to determine soap, present at 0-250 ppm in used frying oils. The test depends on the

The *FRI Test* is another colorimetric test, sensitive to carboxyl compounds, which also gave quite good correlations with other tests (Croons *et al.*, 1986).

TABLE 1. ANALYSIS OF USED OILS THAT FOAMED
(Perrin *et al.*, 1985)

Sample	GN1	GN2	SF	GN3	GN3*
Number of fryings	28	20	21	25	10
Polar glycerides (% of total glycerides)	28.4	32.8	30	32.8	17.2
Polymeric glycerides (% of total glycerides)	21.5	21.2	20	25	10.4
Dimers (% of polymeric glycerides)	60	56	64	56	75
Higher polymers (% of polymeric glycerides)	40	44	36	44	25

* sampled before stable foam formation.

colour formed in the aqueous layer after the oil is shaken with a solution of bromophenol blue in aqueous acetone. In a second paper Blumenthal *et al.* (1986) show that the alkaline material is mainly sodium soap, formed by interaction of some components of the food-stuff being fried with the oil.

Viscosity. Increases in viscosity, measurable by any usual method, result from the development of polymers. Higher viscosity oils will drain less well from food products.

'Rau' Test. This test is done with a colorimetric kit marketed by Walter Rau Hilter, West Germany; it depends on colour changes when the oil is mixed with a solution of redox indicators. It is said (Meyer, 1979) to correlate very well with the petroleum ether insoluble oxidized acids. It correlated well with the determination of total polar compounds according to Guhr *et al.* (1978), when 100 restaurant samples were examined (Croon *et al.*, 1986).

The *Food Oil Sensor* provides an instrumental measure of dielectric constant. It has been found useful by a number of workers (including those at PORIM). Its disadvantage is that different unused oils give different readings. Therefore it is necessary to obtain a 'zero' reading with the oil in use. Furthermore some changes in frying fat have a negative effect, others a positive, and moisture also affects the readings.

Nonetheless Croon *et al.* (1986) found it to give a good correlation with total polar compounds. It is probably most useful in monitoring quality in a production unit which uses the same oil for the same type of food product for long periods. For results consult, for example, Paradis *et al.* (1981). The instrument is described in Food Technology 1979, pp. 50—57.

Saponification Colour. This long-established method has recently been described as more reliable than the determination of 'oxidized fatty acids' and as an excellent rapid

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