the carbon rod technique is not as reliable for these elements as the direct aspiration or char ashing techniques. It was concluded that copper, iron, manganese and sodium can be determined with equal success using any of these three methods.

Farhan and Pazendeh (10) report that direct and simultaneous determinations of iron, copper, nickel, lead, silver, aluminum, magnesium, calcium and manganese can be obtained using arc spectrography. This method has a reported repeatability of ± 10% based on spectra from three replications of a given sample.

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Measurements of Frying Fat Deterioration: A Brief Review

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ABSTRACT

Many factors affect the rate of deterioration of a fat used for deep fat frying. Because of the complexity of the problem, there is no single procedure which will yield reliable results in all situations. Determination of total polar materials in a frying fat provides the most reliable measure of the extent of deterioration in most cases. For monitoring a frying operation in which there is no dilution of the frying fat by the fat in the food being fried, the change in the dielectric constant is the simplest of the methods judged reliable. Free fatty acid determinations by titration and peroxide value are not recommended procedures for measuring frying fat deterioration.

INTRODUCTION

In deep fat frying, a complex series of changes and reactions produce numerous decomposition products. The complexity is illustrated in Figure 1. A list of methods for evaluating fat deterioration is provided in Table I. As these reactions proceed, the functional, sensory and nutritional quality of frying fats are changed and may reach a point where high quality foods can no longer be prepared. The question is, how does one know when the frying fat needs to be dumped? Unfortunately, there is no simple answer. Many different foods are fried in various fats using a choice of fryer designs and operating conditions. The combinations of these variables determines the rate at which the individual reactions take place. For example, in one operation, the rate of hydrolysis may be twice that of the rate of oxidation, whereas in another operation, the reverse may occur. Hence, a specific method may be ideal for one operation but completely useless in another. Determination of the endpoint of a frying fat requires good judgment, based on knowledge of the particular frying operation, the nature of the deep frying fat, and the advantages and limitations of the analytical procedures employed.

DISCUSSION

The first attempt to define a deteriorated frying fat was made by the German Society for Fat Research in 1973 (1). It was recommended that "a used frying fat is deteriorated if, without doubt, odor and taste are unacceptable; or if, in case of doubtful sensory assessment, the concentration of petroleum ether insoluble oxidized fatty acids is 0.7% or higher and the smoke point is lower than 170 C; or if the concentration of petroleum ether insoluble oxidized fatty

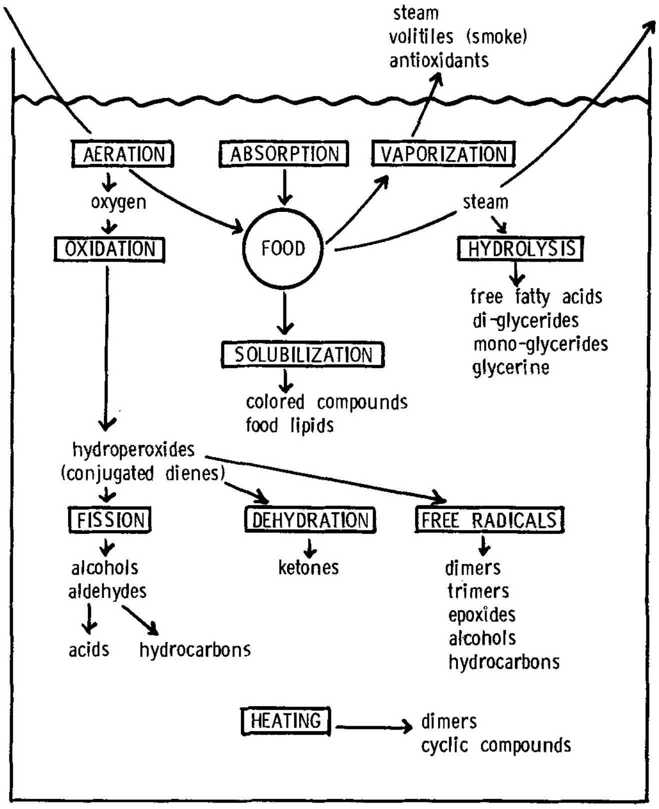

FIG. 1. Changes occurring during deep fat frying.

TABLE I

Methods for Determining Fat Deterioration

Method	References
Free fatty acids	8-10
Peroxide value	6,8,9,11
Iodine value	6,8,9
Dienes	6,12
Refractive index	9,13,14
Viscosity	9,14
Color	7,9,14
Carbonyls	13
Kreis test	12,13
TBA test	13,14
Anisidine value	12
Non-urea-adduct forming esters	9
Oxirane compounds	15
Petroleum ether insoluble oxidized fatty acids	4,5
Total polar materials	3-6
Dielectric constant	6

acids is 1.0% or higher." A similar statement was subsequently published by the Chemists of the German Health Ministry (2). Although taste evaluations in any food operation is the most important quality measurement, taste evaluations are unreliable for routine quality control testing. It is always preferred to have a quantitative method for which the rejection point was established using formal, sensory evaluations. The petroleum ether insoluble oxidized fatty acids are determined by saponification of 5 g of fat, acidification, extraction with ether, evaporation of the ether, extraction with petroleum ether (bp 30-50) and weighing the residue. The method requires considerable skill and is time-consuming. Much work has been done, especially in Germany, to find suitable alternate methods.

Determination of total polar materials (3-6) appears to be emerging as the best substitute for the petroleum ether insoluble oxidized fatty acid method. Total polar materials are determined by dissolving the fat in a relatively nonpolar solvent such as toluene or benzene and running it through a silica gel column which adsorbs the polar compounds. After evaporation of the solvent, the nonpolar fat can be weighed and the total polar materials estimated by the difference, or the total polar materials can be determined directly by eluting them from the column with ether or a mixture of chloroform and methanol. It has been shown that ca. 27% of total polar materials correspond to ca. 1% of petroleum ether insoluble oxidized fatty acids (4,5).

Northern States Instrument Corp. (Lino Lakes, MN) developed an instrument which measures the dielectric constant of insulating liquids. The instrument is a compact unit, is relatively inexpensive, is simple to operate and requires only a few drops of oil for each measurement. For the evaluation of frying fats, the instrument must be first calibrated with the fresh oil used in the frying operation before the used oil can be checked. Fritsch et al. (6) evaluated the instrument. A soybean oil (SBO), an animal-vegetable shortening (AVS) and a hydrogenated vegetable shortening (HVS) were heated at 190 C for 8 hr each day for 4 days with and without the frying of potatoes. Samples of used fat were taken at the end of each day and the instrument readings compared to other analyses. A summary of the data is shown in Table II. The initial AOM stabilities of the fats were 10, 65 and 200+ hr for the SBO, AVS and HVS, respectively. It was therefore anticipated that the rate of deterioration would follow the same order. Only three of the eight tests clearly showed this relationship. The tests were for total polar materials, change in the dielectric constant (instrument reading), and decrease in iodine value. In both the SBO and the HVS, the increase in total polar materials and instrument reading was about the same when the fat was just heated or when potatoes were fried in the fat. This was not true for the AVS, in which the total polar materials and the instrument reading increased more slowly when the fat was heated only than when it was used for frying. This difference was attributed to the BHA and BHT in the AVS. When potatoes were fried in this fat, the antioxidants were lost by steam distillation; hence, the antioxidants provided little or no protection in the frying experiment but they provided significant protection when the fat was just heated.

No relationship was observed between the increase in free fatty acids of the three fats and their anticipated stability. This was expected. AOM stability measures resistance to oxidation. Oxidation produces acids; however, in deep fat frying, acids also are produced by hydrolysis—the reaction of fat with water to form free fatty acids (FFA), di- and monoglycerides and glycerine. Hydrolytically generated FFA up to at least 2% from nonlauric acid oils, e.g., soybean, cottonseed, peanut and palm oils, have no adverse effect on the odor or the flavor of foods. However, the FFA of lauric acid oils, such as coconut oil, will produce a soapy flavor at ca. 0.5%. For this reason, lauric acid oils are used only for the deep fat frying of low-

TABLE II

Analytical Results of Fats Heated (H) or Used for the Frying (F) of Potatoes for 32 Hr at 190 C

Initial	Soybean oil		Animal-vegetable shortening		Hydrogenated vegetable shortening	
AOM (hr)	10		65		200+	
Iodine value	122.8		49.3		70.2	
FFA	0.02		0.05		0.02	
Antioxidants	None		BHA+BHT		None	
Change in	(H)	(F)	(H)	(F)	(H)	(F)
Polar materials	18.7	18.4	6.0	13.5	3.6	3.9
Free fatty acids	0.15	0.28	0.18	0.73	0.07	0.36
Color	0.83	4.10	0.34	1.02	0.31	1.34
Iodine value	- 8.1	- 4.5	-2.1	- 3.2	-0.6	-0.9
Peroxide value	8.6	21.6	7.9	13.6	1.3	3.0
Dienes	0.26	0.29	0.11	0.07	0.10	0.11
Instrument reading	5.1	6.0	1.7	3.8	1.1	1.0

moisture foods, such as the roasting of nuts. The products of hydrolysis have no adverse effect on the nutritional quality of a food. Some of the factors which affect the rate of hydrolysis are unknown; however, the higher the initial FFA, the greater will be the amounts of FFA formed by hydrolysis (7). In most deep fat frying operations, the amount of FFA produced by hydrolysis is too small to affect the quality of the food. Generally, the adverse effects are due to oxidation. Because the determination of FFA by titration does not differentiate between acids formed by oxidation and those formed by hydrolysis, the increase in FFA is a poor measure of frying fat deterioration. High correlations can be obtained between FFA and other measures of deterioration. For example, the correlation coefficient between FFA and total polar materials in the frying of potatoes for the SBO was 0.987, for the AVS 0.979, and for the HVS 0.913. However, when the data from all three fats were combined, the correlation coefficient was only 0.687 and would be even lower if the data from heating without frying had been included. The author has never seen a deep fat frying operation in which the rate of hydrolysis and the rate of oxidation always remains the same. Hence, when FFA are used to monitor an operation, the probability is high that fat which is perfectly acceptable will be frequently dumped and that, now and then, fat which should have been dumped will be used for frying.

Coloring of fats increased more rapidly when potatoes were fried than when they were just heated. This was because browning pigments from the food were dissolved into the frying fats. The color of the SBO increased the most and that of the AVS the least. When polyunsaturated fatty acids are oxidized, a shift in one of the double bonds occurs producing a conjugated diene that can be measured by UV absorption. The greatest change in the diene content was found during the first day of the tests. The changes during the subsequent days were relatively small. Foam height also was measured; however, the results were inconsistent.

Peroxides under deep fat frying conditions are unstable. Another problem is that the peroxides may increase after the sample is taken from the fryer, before it is analyzed. This can be controlled, but is difficult in a commercial frying operation. Because of these factors, the author does not recommend peroxide values for measuring frying fat deterioration.

The change in the dielectric constant was a good indicator of the extent of deterioration obtained in three different frying fats deteriorated both by frying potatoes and by heating without frying. The correlation coefficients between the instrument readings and results of other methods on the combined data are shown in Table III. This procedure is very simple and results can be obtained in a matter of minutes. Yet, it also has limitations. The dielectric constants of different fresh fats are not the same. Generally, the more saturated fats will have a lower value than the highly unsaturated fats. Hence, the instrument can only be used when a sample of fresh fat corresponding to the used fat is available. When the instrument is used to monitor a frying operation, results are obtained problem-free, depending on the type of food used. During the frying of some foods, such as chicken, some of the fat in the food is extracted by and into the frying fat. If the food fat has a lower dielectric constant than the frying fat, a negative reading would be obtained, but the increase would be less than the extent of the deterioration. If the food fat has a higher dielectric constant than the frying fat, the reverse would happen.

TABLE III

Correlation between Change in Dielectric Constant and Other Analyses of the Combined Data of Three Fats with Different Stabilities Deteriorated Both by Frying Potatoes and by Heating without Frying

Analysis	Number of samples	Correlation coefficient
Total polar materials	24	.991
Decrease in iodine value	18	.947
Color	24	.785
Peroxide value	24	.773
Diene content	24	.745
Free fatty acids	24	.569

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