A Gas Chromatographic Method for Continuous Accelerated Study of 0_2 Uptake in Fats[1]

THERE ARE MANY METHODS for determining oxidation of fats in foods by accelerating conditions and determining some of the reaction products as a function of time. Among these are the manometric techniques which utilize oxygen absorption as a measure of stability. These methods involve measuring changes in pressure or volume of gas in contact with the sample. A major defect of the manometric procedures is that only net pressure or volume changes are measured. Any gas, such as CO_2, produced by the oxidative reaction may cause an apparent reversal of oxygen uptake unless the vessel contains a CO_2 absorbent (1). A direct determination of the composition of the gases above the autoxidized fat should, therefore, provide the most direct measurement of the rate of oxidation of the sample, in addition to any changes in the composition of the gas phase. Gas chromatography provides a convenient, rapid and accurate method for this determination (2,3).

The apparatus used in this method is the Fisher Gas Partitioner, Model 25M, with a Sargent Recorder, Model SR. Helium carrier gas flow rate was 80 ml/min. The gas sample passes successively through a drying tube containing Drierite, a first column of 30% hexamethyl phosphoramide on 60–80 mesh column pack which separates CO_2 and a second column containing Molecular Sieve 13X. Depending upon the oxygen content, the volume of gas sample ranges from 0.01–0.1 ml. The order of elution is CO_2, O_2, N_2, CH_4 and CO. A complete determination of these gases may be carried out in 3–5 min. If the analysis is limited to CO_2, O_2 and N_2, the time is reduced to 1–2 min.

The simplest reaction vessel is a reagent bottle 250–300 cc capacity with a 3 cm O.D. neck closed with a serum bottle stopper. The flaps of the stopper may be further secured around the bottle neck by a rubber band when pressures more than one atmosphere develop in the headspace gases.

Experimental results have shown that at least 25 samples of gas may be withdrawn with a thin needle without leakage in the system. A more widely useful reaction vessel, especially for samples too large to pass the neck of the flask can be made from any can or jar. A hole ⅛ in. in diameter is punched in the lid, and a disc of gum rubber or septum seal ½ in. in diameter (No. 46887 Beckman Cat. 2500) is attached to the top or the innerside with RTV silicone rubber adhesive (GE Silicone Products, Waterford, N.Y.).

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TABLE I

Oxidation Rates

Safflower oil	Surface	Oxidation [a] time, hr
Refined	Paper	185
Refined	Glass	305
Stripped	Paper	7
Stripped	Glass	100

[a] Time for consumption of one-half of the available oxygen.

The oxidation rates of refined safflower oil and the oil stripped of its natural antioxidants (General Biochemicals) were measured. The oils were applied dropwise on 15 cm circles of No. 42 Whatman filter paper until one gram was added. The folded filter papers were placed in 250 ml reagent bottles. Controls consisted of one gram of each oil placed directly in bottles. The bottles were then closed with the rubber serum stoppers described, and were incubated at 50C. Oxygen was determined periodically until half of the available O_2 was used. Table I shows the time in hours.

During the past three years we have used this method in investigating the effects of antioxidants and prooxidants in autoxidation of dehydrated military rations and model food systems in accelerated storage. Oxygen uptake and changes in gas compostiion curves may be completed in a few hours or several days, depending on storage temperature.

S. J. BISHOV, A. S. HENICK
U.S. Army Natick Laboratories
Natick, Massachusetts

REFERENCES

1. Umbreit, W. W., R. H. Burris and J. F. Stauffer, "Manometric Techniques and Tissue Metabolism." Burgess Publishing Co., Minneapolis, Minn., 1949, p. 221.
2. Bishov, S. J., A. S. Henick and R. B. Koch, Food Res. *25*, 174–178 (1960).
3. Stahl, W. H., W. A. Voelker and J. H. Sullivan, Food Technol. *14*, 14–19 (1964).

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High Oleic Acid Safflower Oil: A New Stable Edible Oil

DURING RECENT YEARS safflower oil has had increasing use as an edible oil because of its high unsaturation and good quality. Its iodine value (ca. 144) results from a linoleic acid content in excess of 70% and a negligible linolenic acid content. As a cooking oil, however, safflower has not penetrated large markets because it tends to form considerable polymeric materials. The polymers are formed by oxidative, rather than purely thermal, reactions involving the linoleic acid, even though peroxide contents are extremely low while cooking is taking place.

Recently, Knowles and co-workers at the University of California (Davis) have reported a new variety of high oleic acid safflower seed (UC-1) in which the content of oleic acid is almost 80% of the total fatty acids (Table I) (1). We have previously re-

TABLE I

Fatty Acid Contents of Safflower Oils (%)

	UC-1	Commercial (average)
Palmitic	5.4	6.0
Stearic	1.7	4.0
Oleic	80.7	14.0
Linoleic	12.2	76.0

TABLE II

Polymer Formation and Viscosity Changes of Cooking Oils after Oxidation [a]

Oil [b]	Viscosity at 25C				% Polymer after oxidation
	Before oxidation		After oxidation		
	Gardner	Stokes	Gardner	(Stokes)	
High oleic safflower (crude)	B	0.65	H	2.00	29.1
High oleic safflower (deodorized and bleached)	B	0.65	K	2.75	28.4
Commercial safflower	B	0.65	R	4.70	48.1
Commercial safflower (deodorized, not stabilized)	A	0.50	P	4.00	51.0
Commercial soybean	B	0.65	P	4.00	37.0
Commercial cotton seed	B	0.65	M	3.20	37.8
Commercial hydrogenated frying oil	C	0.85 [c]	K	2.75	34.1

[a] Conditions: 185C, air at 200 ml/min for 18 hr.
[b] All commercial oils obtained locally.
[c] Oil was supercooled at 25C.

ported some preliminary studies on this type of seed as well (2). Because linoleic acid, with its methylene group between two double bonds, is the component of ordinary safflower oil most reactive with oxygen, it was anticipated that the UC-1 variety would be considerably more stable towards oxygen than current commercial varieties. We have demonstrated this at high temperature by comparing the oxidative stability of UC-1 oil with that of several commercially available, edible oils.

The oils were tested in a very simple apparatus. A 250-ml three-neck flask equipped with thermometer, capillary bubble tube and outlet tube leading to a dry-ice trap was immersed in a controlled-temperature oil bath kept at 185C ± 1C. An 80-g sample of the oil to be examined was introduced and when the oil temperature reached 180C, compressed air (breathing quality, Ohio Chemical Co.) was bubbled into the oil at 200 ml/min ± 10 ml/min. The air flow and heating were maintained for 18 hr, after which time the oil was cooled and stored under nitrogen until it was analyzed. The various oils examined, their viscosities before and after heating, and the amounts of polymer found are shown in Table II.

Particularly noteworthy is that UC-1, containing only slightly more than 7% saturated acids, compares favorably to the hydrogenated commercial frying oil which contains over 25% saturated acids. Moreover, the very bland, high-oleic oil is liquid at refrigerator temperatures, while the commercial frying oil is solid at room temperature. All the oils darkened during oxidation, but the UC-1 and other safflower oils remained lightest in color after reaction.

At the beginning of oxidation, all of the oils tested had low peroxide value (ca. 1) and these values did not rise significantly throughout the oxidation. Thus, our results agree with those of Hess and O'Hare (3) who showed that peroxide breakdown in linseed oil is so rapid at high temperatures that maximum values are low. Oxygen is necessary for reaction to occur, however. No significant increase in viscosity and no polymer formation was noted in regular safflower oil in which nitrogen was bubbled through at 185C, whether or not water was added [as moist cotton balls (4)] during the heating.

To determine amount of polymer formed in the oils, the triglycerides were converted to fatty acid methyl esters by sodium methoxide–catalyzed transesterification. The product esters were distilled at 0.01 mm of mercury from a flask heated in an oil bath at 185C. Material remaining in the flask was weighed and reported as polymer (Table II). The UC-1 oil formed less polymer than any of the commercial oils, including the hydrogenated frying oil.

This is a severe test which does not correspond to any ordinary conditions of cooking. Our purpose, however, was to devise a means of screening oils for oxidative stability, as well as a means for forming considerable amounts of polymeric and volatile materials for analysis. The method clearly illustrates the differences in various oils under such conditions, and detailed analyses of the volatile and polymeric products will be reported. Related stability studies at lower temperatures are in progress as well.

G. FULLER
G. O. KOHLER
T. H. APPLEWHITE
Western Utilization Research and Development Division
ARS, USDA
Albany, California

REFERENCES

1. Knowles, P. F., A. B. Bill and J. E. Ruckman, Calif. Agr. *19*, No. 12, 15 (1965).
2. Applewhite, T. H., JAOCS *43*, 406–408 (1966).
3. Hess, P. S., and G. A. O'Hare, Ind. Eng. Chem. *42*, 1424–1431 (1950).
4. Krishnamurthy, R. G., T. Kawada and S. S. Chang, JAOCS *42*, 878–882 (1965).

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In Table I, p 377, the data in lines 12 and 13 are in reverse order. The table should read:

Epoxidized linseed oil (Control A)	9.00 [b]	0.11	5.0 [b]	0–1
Epoxidized soybean oil (Control B)	6.60 [b]	0.22	2.7 [b]	1