by argentation TLC followed by gas chromatographic analysis (Ag-TLC/O_3/GC) of the ozonolysis products.

The results of the comparative study are reported in Table XIX. In general, the results compare well, particularly for the shortening sample; however, improvement in the capillary separation is still desirable. Although the capillary analysis requires ca. 2 hr, and is much more time-consuming than any of the previous separations discussed, it is a great improvement over the 1.5-day Ag-TLC/O_3/GC procedure.

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Techniques for Flavor and Odor Evaluation of Soy Oil

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ABSTRACT

Means of evaluating soybean oil for flavor on a "now" basis and on a "predictive" basis are presented. Emphasis is placed on more recent objective methodology for measuring oil volatiles and using their correlation with flavor. Applications of a modified volatile technique for use with soy isolates or soy proteins is shown. The importance of sensory analysis and a summary of methodology currently being used are discussed.

INTRODUCTION

Techniques for flavor and odor evaluation of soybean oil are needed as much today as in previous years, particularly as new extraction and processing changes are evolved due to high energy costs. The consumer also has been conditioned over the years and has become more perceptive of flavor quality.

Taste or organoleptic evaluation will always be the final judgment on flavor and odor, however, there is also a need for more objective methodology to support organoleptic decisions and, at the same time, supply information specific enough to understand and offer a solution to flavor and odor problems.

In this review, techniques for evaluating the flavor and odor of soybean oil are presented on the basis of "now tests" and "predictive tests."

"NOW" TECHNIQUES

Chemical and Physical

Some of the more common techniques for evaluating oil quality related either directly or indirectly to flavor are: peroxide (1), thiobarituric acid test (TBA) (2), Kreis test (3), anisidine test (4), oxirane test (1), conjugated diene and triene (2), conjugable oxidation products (COP) (5), fluorescence (6), infrared spectroscopy (7), polarography (8), and gas chromatography (9-11).

Official status in the USA has been given to only two of these tests, the peroxide AOCS, Cd8-53 and the oxirane test Cd-9-57 (1).

The most frequently consulted of the "now tests" listed here are peroxide, anisidine, conjugated diene and triene, thiobarbituric and volatiles using gas chromatography.

Peroxide Value

The initial and primary products of lipid oxidation are hydroperoxides which are transitory and break down by further reactions. Because of their breakdown to non-peroxide materials, their correlation with flavor can vary considerably. This test lacks specificity, i.e., it does not distinguish between types of fatty acids undergoing oxidation and it does not measure secondary products formed which are responsible for flavor change. Its chief value, then, is a measure of oxidation in its early stage.

Anisidine Value

This test developed by Holm (4) is a measure primarily of α-β-unsaturated aldehydes, and has been shown to correlate well with oxidation and flavor in oils (12,13). Others (14) have questioned its value for oils. The test did show a correlation with flavor deterioration of fats in dried emulsions (15). Holm (4) also introduced the term oxidation value which = anisidine value + 2 times the peroxide value (OV = AV + 2 PV). Using this combination of tests, slightly higher correlations with flavor were obtained.

Research by J.L. Williams in our own laboratory concluded that this test was of little value in measuring oil quality in U.S. soybean oils (unpublished data).

Conjugated Diene and Triene

Formation of hydroperoxide normally is coincidental with conjugation of double bonds in polyunsaturated fatty acids. This conjugation absorbs UV light at a wavelength of ca. 233 nm for diene unsaturation and 268 nm for triene unsaturation. The increase in absorption, however, is difficult to relate to the degree of oxidation because the rates of oxidation vary with the different types of polyunsaturated fatty acids. For a given composition, however, these values can be used as a relative measure of oxidation. St. Angelo et al. (16) have shown good correlation of this test with peroxide values on peanut butter samples.

Thiobarbituric Acid Test

This test was shown to correlate well with the peroxide value in oils containing fatty acids with three or more double bonds (2). Researchers should be careful in applying this test to unknown samples, particularly foods (17,18), where interference in color formation and reaction with components other than malonaldehyde can occur.

Volatiles—Gas Chromatography

Almost all chemical and physical tests presented in the literature for measuring oil quality are indirect measures of flavor. Measurement of volatiles by gas chromatography (GC) for specificity and accuracy has made possible the objective determination of flavor for many foods, ingredients and packaging materials.

A number of procedures have been used in recent years relating volatiles in oils to flavor quality (9-11). The AOCS also has been active in the assessment of some of these procedures and their correlation with oil flavor. A summary of their results to date indicate that all of the gas chromatographic volatile procedures evaluated were more precise than any of the individual taste panels or the combinations of all flavor panels (19).

The volatile procedure developed by the author (11) is outlined next.

Vegetable oil with an added internal standard is distributed over glass wool packed on one side of an aluminum U-tube, 2 ft in length. The tube is then purged with a flow of helium or nitrogen while being heated in a forced air oven for 20 min. Volatiles from the oil are swept out of the tube and are trapped on a 6 ft x 1/8 in. column containing Porapak P, a styrene-divinylbenzene copolymer, which is held at room temperature during the trapping. The gas chromatographic column is then disconnected from the U-tube and reconnected to a gas chromatograph having a flame ionization detector. The GC oven is temperature-programmed, the components eluted and the results integrated, giving a quantitation of each component calculated against the internal standard. Gas chromatograms of representative samples of a soybean oil of good flavor quality and one of fair quality are shown in Figures 1 and 2.

The volatile GC techniques also are useful for analysis of soy flours, meals and protein isolates. Residual lipids have been shown to be a major source of the flavor components that limit the use of soy products (20). Rayner et al. (21) examined soy flours and soy isolates using this technique and Figures 3 and 4 show examples of good and poor flavor soy flours and soy isolates.

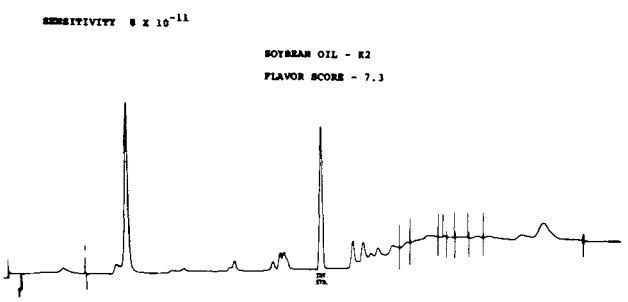

FIG. 1. Gas chromatogram of volatiles eluted from a soybean oil with a good flavor score.

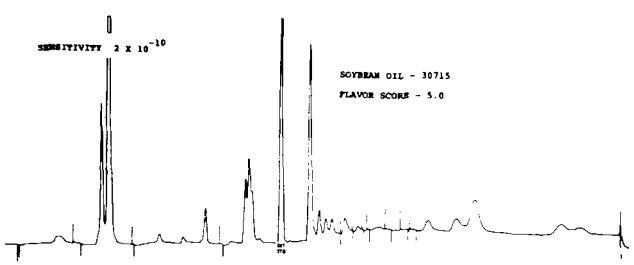

FIG. 2. Gas chromatogram of volatiles eluted from a soybean oil having fair flavor score.

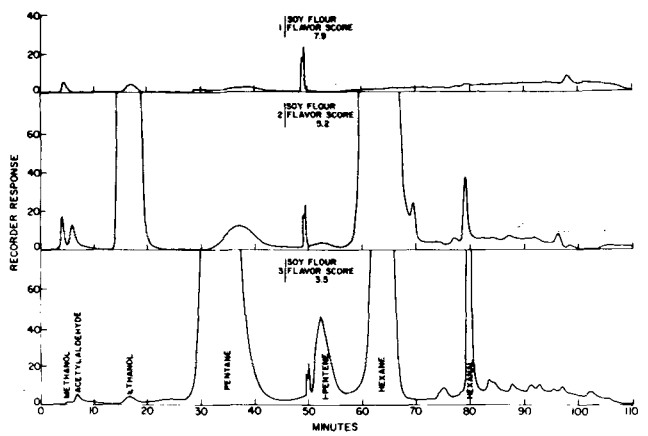

FIG. 3. Profile of volatiles for soy flour, showing the differences associated with flavor scores (21).

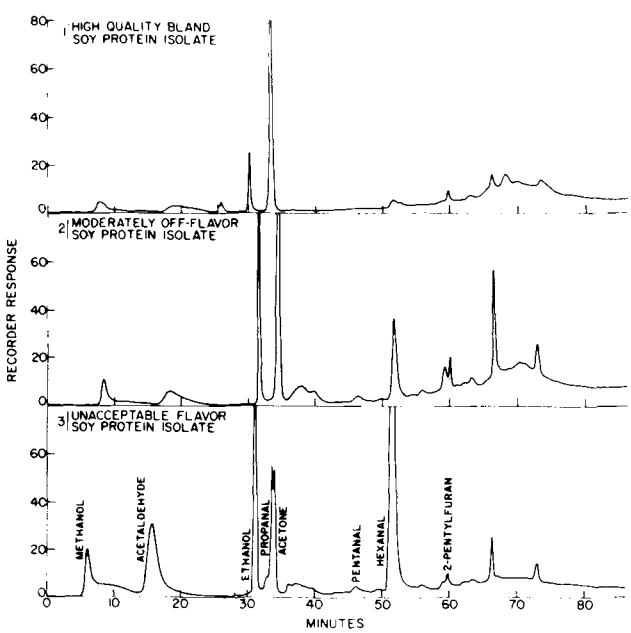

FIG. 4. Profile of volatiles for soy protein isolates (21).

A modification of the U-tube procedure developed in our laboratory also has been applied to soy isolates and soy fermentates. This procedure differs from that used for oil volatiles in that an 18 in. long by 3/8 in. od length of aluminum tubing was used in sample purging. This larger size tubing permits use of up to 2-g samples. The addition of water is necessary prior to purging to achieve recovery of volatiles from the dry soy isolates or flours. Under the conditions used for purging soy isolates, i.e., 120 C and 0.7 ml of water for a 0.6-g sample size, a steam distillation effect probably occurs, releasing the bound volatiles. The sample is purged at 120 C for 30 min with a helium flow of 90 ml/min. Two g of washed and ignited sand are mixed with each sample to give better dispersion prior to adding the water. A cold cloth also is placed at the exit of the U-tube during purging to condense most of the water vapor. This is particularly important when doing further mass spectrometry (MS) work on such volatiles. A typical chromatogram of a soy isolate analyzed using this procedure is shown in Figure 5. A number of the volatile components were identified using GC-MS and are shown in Table I. Two additional samples of soy isolate analyzed by our U-tube procedure and judged organoleptically as having a good and poor flavor are shown in Figures 6 and 7.

ORGANOLEPTIC TECHNIQUES

Organoleptic or taste evaluation will always be necessary and probably will remain the most important technique in flavor evaluation. We may desire to replace the erratic and subjective human senses with objective physical and chemical analytical methods, but the ultimate decision on flavor quality will be made by humans, whose evaluations will always be subjective.

Taste panels for edible oil evaluations are used for two general purposes: first, as a highly trained expert panel used as a research or analytical tool and second, as a panel geared toward consumer acceptance.

The selection of the panel members is quite different. The research panel should consist of people who have demonstrated their ability to discriminate among different oil samples and to give correct intensity levels and descriptions of flavor. The consumer panel should be a random sampling of the people who constitute the market of interest. The remainder of the discussion on organoleptic evaluation will be directed at the establishment of an expert or research taste panel.

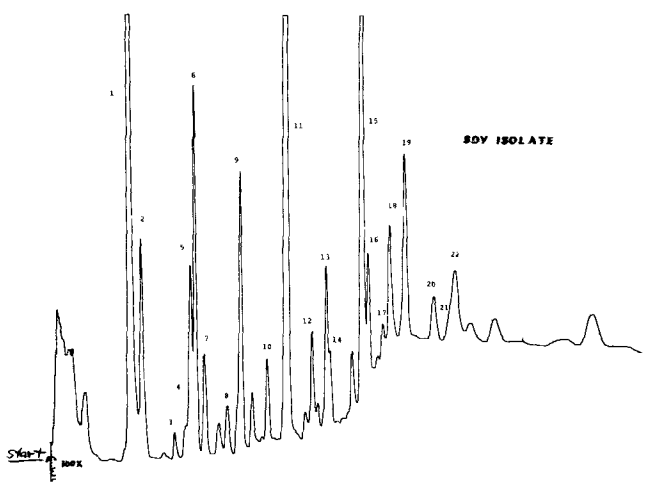

FIG. 5. Volatile profile of soy isolate using the modified U-tube procedure.

TABLE I

Compounds Identified by GC-MS Analysis of Soy Isolate Volatiles[a]

1. Acetone	12. 1-Nexanol
2. *n*-Pentane	13. 2-Heptanone
3. Methyl ethyl ketone	14. Heptanal
4. Butyraldehyde	15. 2-Pentyl furan
5. Diacetyl	16. Benzaldehyde
6. *n*-Hexane	17. Dichlorobenzene
7. Hexene	18. 2-Nonanone
8. Isopentanal	19. Nonanal
9. Pentanal	20. 1-Nonanol
10. 1-Pentanol	21. 2-Decanone
11. Hexanal	22. γ-Lactone

[a]Numbers refer to peaks shown in Fig. 5.

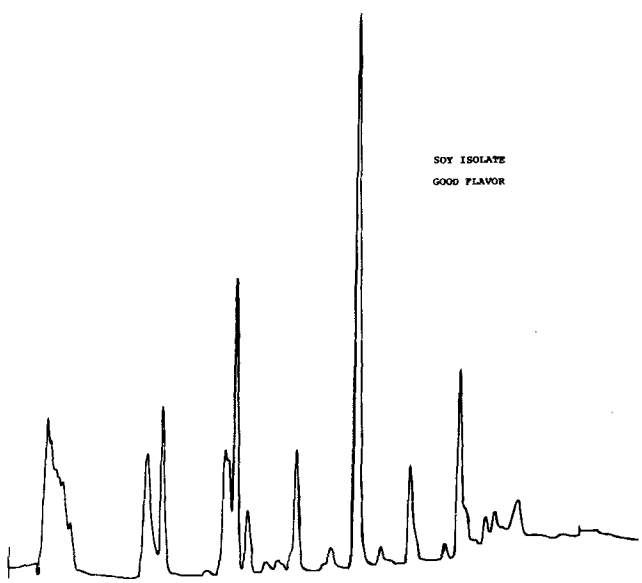

FIG. 6. Volatile profile of soy protein isolate–good flavor (U-tube procedure).

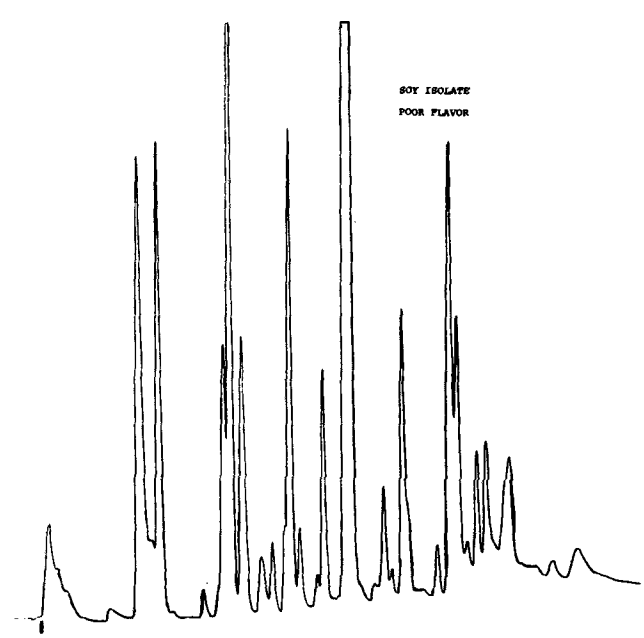

FIG. 7. Volatile profile of soy protein isolate–poor flavor (U-tube procedure).

General Methodology

(a) Taste panels should be conducted in a well ventilated, lighted and air-conditioned room. (b) Each panel member should have a separate booth where, in a comfortable sitting position, s/he would have easy access to samples. Experience has shown that quietness, orderliness and regularity contribute to more accurate evaluations. (c) Odors and flavors of oils are more easily detected if the oils are warm; 50 C is recommended. This temperature should be carefully controlled from sample to sample. (d) Samples should be presented "blind" to the panel, in pairs, for most accurate results but many panels can handle sets of 4 at one sitting. (e) Water at body temperature or slightly higher should be used for rinsing the mouth between samples. No sample should be swallowed. (f) In general, oils with the strongest flavor should be tasted last; this would normally be determined by odor. Some statistical plans require that they be tasted as presented. (g) Human relations are an important part of any taste panel. Rewards at the end of the taste period, e.g., cookies or cake, are helpful. Where possible, sharing of research results can help sustain the interest of the panel members.

Flavor Score Evaluation Forms

There are no official flavor score sheets or procedures for tasting edible oils. Score sheets vary considerably among companies and over time. However, the trend appears to be directed at uniformity, rather than diversity.

Two typical evaluation forms currently used by the Northern Regional Research Center (USDA) and Kraft, Inc. are shown in Figures 8 and 9. Table II lists a flavor grading scale that has general agreement with members of the AOCS Flavor Nomenclature Committee.

Selection and Training of Panel Members

The selection of panel members normally is determined by performance with known samples. The first test to be given would involve the ability to discriminate among known samples of oil. Several samples normally presented in pairs would be used in this test. Those who have discriminated correctly or most correctly are chosen for additional training sessions.

The next training program would emphasize intensity rating as well as discrimination of oil samples.

The last and most complex of the training sessions would involve flavor types or flavor descriptions. Difficulty in preparing known samples with typical flavor types can often complicate this phase of training. Reliance for procuring the different types of flavor is often placed on experienced oil tasters.

Data Analyses

Statistical analyses are tools to explain and interpret the data in light of the variations and probabilities involved. Statistical methods cannot increase the validity of the original data. Experimental statistical design can be important in obtaining maximal information, and consultation with a statistician is certainly recommended prior to obtaining organoleptic results. There are many ways of statistically analyzing data; results usually are obtained, however, by analysis of variance and correlation techniques. Significance of results usually means that if you accept the assumption that the observed differences in flavor score are real, you will only be wrong once in 20 times at a 5% probability level.

Statistical analyses also are important in judging the performance of individual tasters on the panel to insure continued reliability of results.

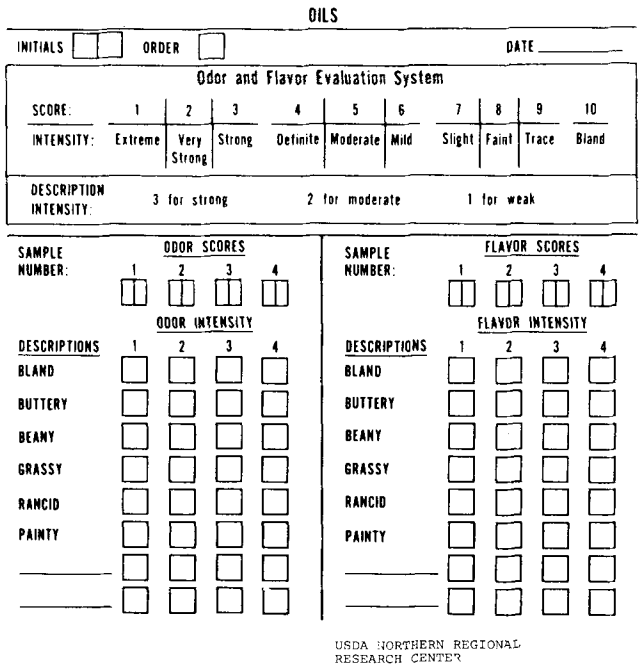

FIG. 8. Flavor score form—USDA Northern Regional Research Center.

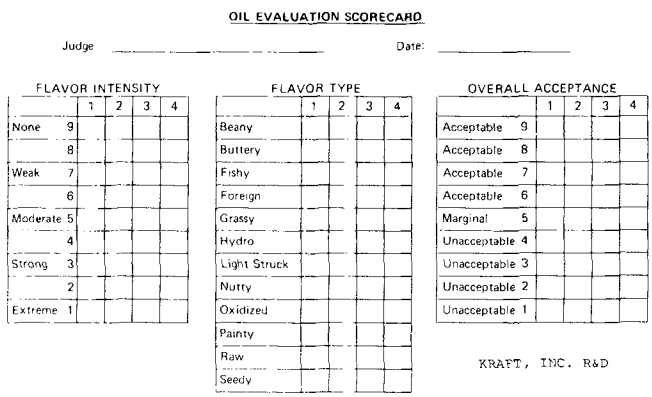

FIG. 9. Flavor score form—Kraft, Inc., Research & Development.

TABLE II

Flavor Grading Scale

Flavor grade	Description of flavor
10	Completely bland
9	Trace of flavor, but not recognizable
8	Sl. nutty, sl. sweet, bacony
7 (fair)	Sl. beany, sl. hydrogenated
6	Sl. raw, sl. oxidized, sl. musty, sl. weedy, burnt
5 (poor)	Sl. reverted, sl. rubbery, sl. like watermelon
4	Sl. rancid, sl. painty
3 (very poor)	Sl. fishy, sl. buggy
2	Intensive flavors and objectionable flavor evaluation
1 (repulsive)	

PREDICTIVE TESTS

The tests most often referred to as predictive, or accelerated, in the literature are the active oxygen method (AOM) (22), the modified ASTM oxygen bomb method (23), the

Eckey oxygen absorption method (24), the Schaal Oven Test (25), and more recently, thermal analysis (26). Only one of these tests, the AOM, has official status for use with edible oil.

General Conditions

The AOM uses 20 ml of oil kept at 97.8 C while air is bubbled through it at 2.33 cc/sec until a peroxide value of 100 meq/kg of oil is attained.

The Eckey oxygen absorption method consists of suspending 1 g of oil on 12.5 g of sand in a closed vessel at atmospheric pressure with air and heating at 80 C until a pressure drop of 40 mm of mercury is reached.

The modified ASTM oxygen bomb method involves the placing of 6 g of oil on tissue paper in a sealed bomb at 50 psi oxygen pressure and at 100 C until a pressure drop of 2 psi/hr is attained.

The Schaal oven test method requires that 50 g of oil be held in a 250-ml beaker with a watch glass on top, and the sample be maintained at ca. 63 C. The samples are smelled daily until a rancid odor is detected. Lea (27) advocated the use of the peroxide value of 70-120 as the endpoint, and the use of a smaller sample.

Thermal analysis is a term used for a series of techniques which measure some physical or chemical change in a material as a function of temperature. This change is measured by a transducer which converts the change into an electrical signal.

The two techniques used with edible oils are differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC measures the amount of heat going into and out of a sample as a function of temperature; its measure of the oxidation process then would be through the exotherm created by the degradation in the oil. TGA measures the change in weight of the sample as a function of temperature and the measurement of oxidation would be through the weight gain of the sample from the oxygen uptake, minus any losses due to decomposition.

Both techniques do correlate with AOM according to Hassel (26). Cross (28) compared DSC in an isothermal mode to the AOM test, showing a correlation of 0.97. Samples requiring 14 days with the AOM procedure were evaluated in less than 4 hr using DSC. Buzas (29) also showed good correlation with oxidative changes using thermal analysis.

DISCUSSION

After reviewing the chemical and physical tests available for measuring oil quality, I conclude that, although each test may have merit, there is not one test that will guarantee correlation with flavor quality. Indeed, all the tests combined would not likely show this correlation on an edible oil of unknown history.

The value of chemical and physical tests, then, lies in the measurement of oxidation or its by-products in oil with a known history, i.e., type and origin of the oil, processing conditions, storage conditions (temp., light, dark), and presence of additives (antioxidants, chelating agents).

Final proof of the value of chemical and physical testing for flavor will ultimately have to be related to sensory evaluation done by a trained panel. Excluding a trained sensory panel, which can be time-consuming and requires a relatively large sample for tasting, volatile-GC measurement techniques appear to be the most promising methods for maximal information on oil quality.

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