A Quality Control Procedure for the Gas Liquid Chromatographic Evaluation of the Flavor Quality of Vegetable Oils[1]

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ABSTRACT AND SUMMARY

An objective procedure which is relatively simple and rapid is under study for the determination of the flavor quality of vegetable oils. This procedure utilizes the direct injection of an oil sample to which has been added an internal standard, into a packed precolumn of a gas chromatograph. The volatiles are swept from the precolumn through a 10% SE-30 column under operating parameters which permit complete elution of all volatiles and internal standard within 20 min. Some 15 to 20 samples can be evaluated in one day before it is necessary to replace any part of the foot-long precolumn. Evaluations have been made by the gas liquid chromatographic (GLC) procedure and by a flavor panel of oil samples subjected to a variety of storage conditions. Generally, differences in the GLC pattern are reflected in the flavor panel results.

INTRODUCTION

Some of the earliest work of the gas liquid chromatographic (GLC) evaluation of flavor of vegetable oils was reported by Scholz and Ptak. Their published report (1) indicated an overall correlation between the ppm pentane obtained by the GLC and the flavor scores based on a ranking system, but not a point to point correspondence with the pentane concentration. This is evident in the scatter of the data presented in Figure 3 of their paper. They also noted that an independent correlation must be established for each oil type.

More recently Dupuy et al. have reported excellent correlations with flavor panels of a wide variety of food materials (2-8). Duplication of Dupuy's system was found to require special equipment and, as his technique matured, longer and longer analysis times (3-8). Since it was felt that there was a need for a more rapid analysis for use as a quality control tool, the following approach was taken.

EXPERIMENTAL PROCEDURES

Gas Chromatography

A Beckman GC-65 with a flame ionization detector and outfitted with a U-shaped stainless steel column 5 ft x 1/4 in. OD packed with 10% SE-30 on 80/100 mesh chromosorb W, high purity (HP) was used. Attached to this column was a glass precolumn 1 ft x 1/4 in. OD packed with chromosorb W, (HP) without a liquid phase. The top 3 in. of the precolumn was packed only with silanized glass wool. The column was prepared by first placing a small plug of silanized glass wool at the bottom end and adding carefully 1 g of chromosorb W (HP) to the column using a small funnel with a 4 cm stem length and a 2.5 mm ID. An orange stick 6 in. long with a pencil mark at midpoint was placed in the column so that it rested lightly on the packing. The column was then tapped gently on the laboratory bench until the 3 in. mark on the orange stick coincided with the top end of the column. The 3 in. space was then lightly packed with silanized glass wool. The glass precolumn and the metal column were carefully attached with swagelok fittings and graphite ferrules and conditioned for 2 hr at 200 C. Thereafter operating conditions were as follows: Injection port 230 C; Column 180 C; Detector 230 C; Helium flow 55 ml/min; Hydrogen flow 45 ml/min; Air flow 300 ml/min; sensitivity at 4.0 x 10^{-11} amps full scale at a chart speed of 0.5 in./min.

Sample Preparation

The samples were prepared for injection by first taking an aliquot containing 10 mg of the internal standard, n-octadecane, from a 10 mg per ml stock solution in hexane and transferring it to a 6 oz wide-mouth jar which can be fitted with an airtight cap. The solvent was first completely evaporated under a stream of nitrogen with application of gentle heat, and, when the jar was cool and dry, 100.0 g of a vegetable oil were weighed into it on a top-loading balance. The jar was swirled but not so vigorously as to whip air into the mixture and a 1 μl sample was injected directly into the precolumn. Since the internal standard is a stable compound, the sample jars with the standard were prepared in advance and stored under nitrogen in a freezer. This reduced sample preparation time to less than 5 min between the receipt of an oil sample and the injection of the final 1 μl sample into the gas chromatograph.

TABLE I

(Evaluation of Corn Oil Subjected to Abuse
(Air-Light-Heat Abused at 95 F)

Time (weeks)	Flavor strength (adjusted means)[a]	Flavor pleasantness (adjusted means)[a]	Volatiles ppm
0	4.10	4.80	20
6	4.42	5.87	71
8	5.37	5.42	133
10	6.20	6.05	200
12	5.80	6.44	199
14	4.78	5.78	336
16	5.92	6.04	255
21	6.64	7.21	363
25	7.36	8.07	577
35	7.50	7.86	567
45	7.57	8.21	978

[a] Flavor scores were adjusted for any individual panelist's statistically proven bias in the balanced incomplete block design used for the panel evaluations.

TABLE II

Statistical Evaluation of the Correlation of Gas Liquid Chromatographic (GLC) Total Volatiles vs. Flavor Panel Scores[a]

Corn oil flavor evaluation		R	R^2
(a)	Air-light-heat abused oils		
	Flavor strength	0.83	0.69
	Flavor pleasantness	0.89	0.79
	Product FP x FS	0.89	0.79
(b)	Dark storage oils		
	Flavor strength	0.67	0.45
	Flavor pleasantness	0.69	0.48
	Product FP x FS	0.74	0.54

[a] Correlation coefficient (R) and coefficient of determination (R^2).

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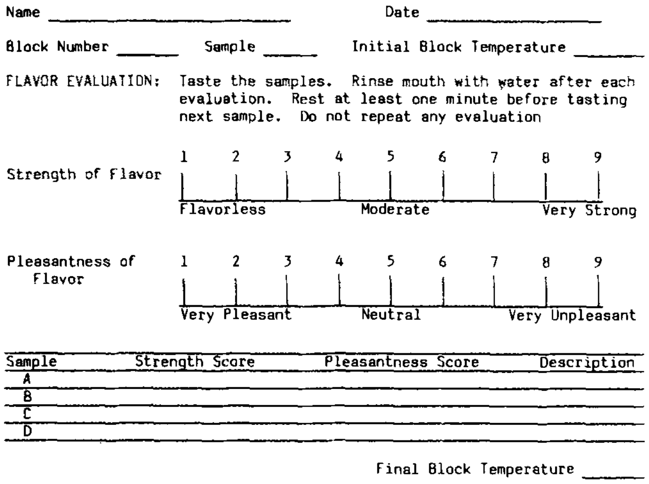
[1] Presented at the AOCS Meeting, New Orleans, April 1976.

TABLE III

Corn Oil Samples–Controlled Temperature Storage

Temp. (°F)	Time Week	Flavor strength	Flavor pleasantness	Volatiles ppm
Initial sample		4.10	4.80	20
0	8	4.37	5.70	35
	12	4.54	5.29	29
	25	4.37	4.89	42
	35	4.83	5.41	31
75	8	4.64	5.50	41
	12	5.14	5.73	44
	25	4.45	5.41	41
	35	5.41	5.73	40
95	8	5.91	5.59	44
	12	5.04	4.94	35
	25	5.68	6.36	46
	35	5.64	6.04	55



Name ______________ Date ______________

Block Number ______ Sample ______ Initial Block Temperature ______

FLAVOR EVALUATION: Taste the samples. Rinse mouth with water after each evaluation. Rest at least one minute before tasting next sample. Do not repeat any evaluation

Strength of Flavor 1 2 3 4 5 6 7 8 9

Flavorless Moderate Very Strong

Pleasantness of Flavor 1 2 3 4 5 6 7 8 9

Very Pleasant Neutral Very Unpleasant

Sample	Strength Score	Pleasantness Score	Description
A			
B			
C			
D			

Final Block Temperature ______

FIG. 1. Flavor Panel Evaluation Form.

Product Evaluations

Three separate storage studies were initiated using corn oil. A supply of bottled corn oil from a single lot was obtained and stored in closed cases at 0 F, 75 F, and 95 F. A second program utilized the same oil supply but stored the samples in a MacBeth light box in a 95 F storage room. For this latter group, the caps were removed and an incident light of 200 candlepower was left on continuously. The third group involved samples drawn from the retains of three processing plants covering a span of time of almost 2 yr. Oil samples were removed in accordance with the schedule indicated in Tables I and III. These were subjected to organoleptic and GLC evaluations.

Flavor Panel

The flavor scores were obtained using a panel specifically trained to flavor oils. The oil samples were presented to the panel in small glass cups in heated aluminum blocks at 60 C and no more than four samples were evaluated at any one sitting. Figure 1 is a representation of a flavor evaluation form with the scales of strength and pleasantness of flavor. This approach to flavor evaluation was proposed by Blumenthal (9). Whereas the strength scale is a continuum, pleasantness has a neutral center point which is the optimum point for flavor pleasantness of an oil.

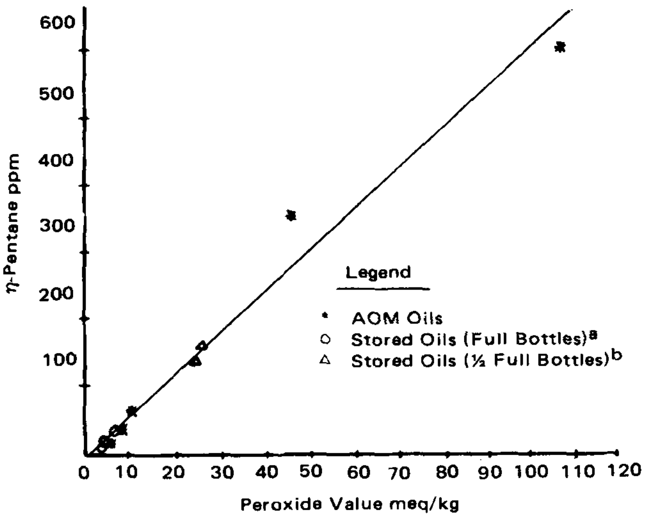


FIG. 2. The Relationship of Pentane, Peroxide Values, and Flavor of Corn Oils. Flavor score based on 5 = excellent and 1 = terrible. (a) Flavor scores in the order of increasing PV (3.45, 3.70, 3.90); (b) Flavor scores in the order of increasing PV (2.35, 3.50).

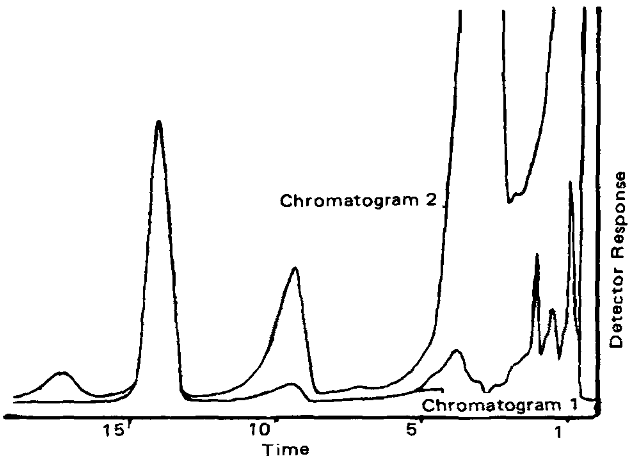


FIG. 3. *Chromatogram 1:* Corn Oil stored at 0 F for 8 wk in a sealed bottle in the dark. *Chromatogram 2:* Corn Oil stored in an open bottle at 95 F for 45 wk in the presence of light and air.

RESULTS AND DISCUSSION

Our studies of the gas chromatographic evaluation of flavor of vegetable oils began in 1965 when a private communication from the Continental Can Company (Scholz and Ptak) indicated that the GLC measurement of hexanal was a measure of the development of rancidity in vegetable oils. Our unreported work which paralleled that of Scholz and Ptak involved the direct injection on a (6 ft x 1/4 in. 10% SE-30 on Diatoport S, 80/100 mesh) nonpolar GLC column of 1 μl of a 1 ml oil sample to which 1 μl of n-octane had been added as an internal standard. While we confirmed that the hexanal peak did increase with abuse of the oil, it was observed that another peak identified as pentane showed greater development with time and temperature abuse of the oil than hexanal. Our initial studies involved a corn oil which was intentionally abused for various times in the active oxygen method (AOM) equipment. While there was seemingly good correlation of the GLC data to the peroxide development in the oil and in other oils stored in both half full and full bottles at 95 F for 4 mo, there was no correlation with the flavor panel scores (Fig. 2).

The publication of Scholz and Ptak (1) and our lack of success led to abandonment of the project until Dupuy and coworkers reported their work in 1971 (2). Since it was observed that, in all of Dupuy's papers in which he had indicated total volatiles (7-8), this measure was reported to

TABLE IV

Correlation of Transformed Flavor Panel Scores of Dark Storage–Corn Oils Relative to Gas Liquid Chromatographic (GLC) Total Volatiles (ppm)[a]

GC (ppm)[a]	FP x FS + 10[b]
35	35
29	34
42	31
31	36
41	36
44	39
41	34
40	41
44	43
33	35
46	46
55	44
20	30

[a] GC = gas chromatography.

[b] δ% Flavor Panel evaluations of Flavor Pleasantness (FP) and Flavor Strength (FS)

have fairly good to good correlations with the flavor ratings (with correlation coefficients from 0.7-0.9), it was decided that a viable approach might involve the elution of the volatiles as a group of merged peaks. An internal standard which would elute much later would provide the means for quantification and a precolumn would be used to trap the oil. We had already used such a system (presented in the experimental section) for the detection of heat exchange fluids or solvents in oils which involved direct injection of oils into a gas chromatograph.

Typical chromatograms of two extreme corn oils are shown in Figure 3. Elution time of the internal standard is 14 min. It is separated by at least 4 min from any of the preceding peaks. There is only one peak present in oils intentionally abused which comes at a later time (18 min) and its elution is complete by 20 min. Injection of the next sample can be made at that point, or as soon as the integrator or computer used will permit. Since such extensively abused samples are the exception, samples can generally be analyzed at a rate of three an hour without difficulty. It has been possible to run about fifteen samples through the system before the glass wool requires replacement and about sixty samples over 4 or 5 days (when the glass wool was changed each night) before the precolumn packing required changing. The latter change involves the removal of packing from the column, repacking and then reconditioning for 2 hr at 200 C. Since experience should permit better understanding of the saturation rate of the precolumn,exchange of the precolumn might be made in the future at a convenient predetermined point. There is never any danger of contaminating the chromatographic column if the operator is cognizant of the warnings given by the system. The internal standard peak indicates the need for a change in glass wool by losing its Gaussian shape with the onset of tailing. When such tailing is also accompanied by a significant increase (ca. 1 min) in retention time, then the precolumn packing also requires replacement.

Calculations have been made according to the formula:

$$\text{GLC Volatiles} = \frac{A_S \times W_{IS}}{A_{IS} \times W_S} \times K$$

A_S = area of chromatogram excluding internal standard
A_{IS} = area of internal standard
W_{IS} = weight of internal standard
W_S = weight of oil
K = instrument response factor

The instrument's response factor (K) can be taken as 1.0 when using a flame ionization detector.

The most dramatic differences were found in the combined air-, light-, and heat-abused samples. However, even though the GLC values more than tripled in 6 wk as shown in Table I, it required a span of about 20 wk before really significant changes were evident in the flavor panel scores.

A statistical analysis of the data from the air-, light-, and heat-abused samples indicates in Table II a reasonable correlation of the GLC values with the strength and the pleasantness as well as the product of these two flavor values. The product of strength and pleasantness was proposed as a way to provide one composite value for flavor and to expand the flavor scale while still giving equal weight to both flavor characteristics.

Table III shows the data of the set stored in closed containers in the dark. The same form of statistical analysis was applied and while the correlation is not as good as the samples intentionally abused under controlled conditions, the product value again has the highest correlation (0.74) as shown in Table II. The poorer correlations with sealed samples are believed caused by some variability in the integrity of the package. For example, the tightness of the cap. The samples which had been assayed by GLC and the flavor panel had not come from identical bottles but from pairs drawn from the same case at the same time. It was observed, however, that the transformation of the product value (FP x FS) by the addition of 10 gave values for the dark storage oils which were in the same order of magnitude as the ppm of the volatiles from the GLC (Table IV).

The final study, that of the product drawn from different locations, initially did not yield a positive correlation. Further evaluations of these production retains were made to break out the effects of some of the variables such as differences due to the three plant locations and a multiplicity of variations in the storage procedures to which the samples had been subjected. The results of samples from two of the plants proved to be linear but slightly displaced from one another. The data from the third plant was spread randomly over the full range of values which apparently was the result of a less controlled retain storage program. This illustrates what should be recognized as a requirement of many of the GLC procedures reported in the literature. Samples have to be treated under the conditions of preparation and storage reported for any equations of correlation to be valid.

If the unknown factors can be more completely resolved to provide correlations as shown in the controlled storage programs, a computer can generate a predictive equation from the data which will provide an estimate of the flavor panel score from the GLC determined ppm total flavor volatiles. Such an equation generated for the flavor pleasantness of corn oil when stored in the dark is flavor pleasantness = 4.144 + 0.0349 (ppm GLC total volatiles). It is believed unlikely that this equation will holdfor other oils or other storage conditions. Therefore, continued study is planned involving other oils and blends so the limitations and advantages of this analytical procedure can be more fully evaluated.

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