KOREAN J. FOOD SCI. TECHNOL.
Vol. 20, No. 5, pp 732~735(1988)

Gas Chromatographic Determination of Flavor Stability of Cooking Oils

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Abstract

Flavor stability of cooking oils such as rice bran oil, double fractionated palm olein and soybean oil were determined by headspace analysis using gas chromatography. In the headspace, the contents of volatile compounds, oxygen and hydrogen were measured. The hydrogen content in the headspace correlated well with the contents of volatile compound ($r > 0.95$). Therefore, it is proposed that a single measurement of hydrogen and oxygen is used as a index of flavor stability of cooking oils instead of separate measurement of volatile compounds and oxygen, which have conventionally been used.

Key words: gas chromatography, flavor stability, headspace analysis, cooking oil

Introduction

One of the important qualities of cooking oil is flavor stability, which is greatly influenced by the characteristics of oils and by the minor components present in oils[1-3].

There have been many assessments to elucidate the analytical methods for the determination of flavor quality and stability of oils[4,5], and are reviewed[6]. For the determination of flavor stability of oils by headspace analysis using gas chromatography, the samples of headspace of oils have been repeatedly injected into gas chromatography to analyze the volatile compounds and molecular oxygen contents using different gas chromatography columns[3,7].

This paper reports a new index for the determination of flavor stability of cooking oils using gas chromatography.

Materials and Methods

Materials

Refined, bleached, deodorized(RBD), and winterized rice bran oil and RBD soybean oil were purchased from local markets in Korea, and RBD double fractionated palm olein in Malaysia. All reagents used were of analytical grade unless otherwise specified.

Storage of oil samples

Fifteen grams of experimental sample were transferred into a 50m*l* serum bottle and air-tightly sealed with a Teflon-coated rubber septum and an aluminum cap. The samples were stored at 60C in a forced-draft air-oven.

Flavor stability measurement

The flavor stability of oils were determined by a combination of volatile compound formation and molecular oxygen disappearence in the headspace of oils in air-tightly sealed bottles. Gas chromatography used for headspace analyses was Hewlett-Packard GC HP-5880. The analytical methods were essentially the same as described by Yoon and Min[7].

Results and Discussion

The gas chromatographic analyses of volatile compounds in the headspace of oil sample showed that the major compounds are butane, pentane,

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propanal and hexanal, according to Mass Spectra, which are reported as products of lipid oxidation[8].

The contents of total volatile compounds in the headspaces of DF palm olein, rice bran oil and soybean oil are shown in Table 1. The total volatile compounds in the headspaces of all oil samples increased as storage days increased. The total volatile compounds in the headspace of DF palm olein increased from initial value of 27,000 to 181,000 whereas those of rice bran oil and soybean oil increased to 530,000 and 1,019,000 after 20 days storage at 60℃, respectively. The results showed that DF palm olein is most stable during storage, and rice bran oil and soybean oil were less stable in decreasing order. It is well known that the flavor quality decreases as the volatile compounds in oils increases[5].

The gas chromatograms of molecular oxygen in the headspace of soybean oil are shown in Fig. 1. The oxygen content decreased as the storage time increased from 0 to 20 days at 60℃, and are shown in Table 1. By the gas chromatography system used for oxygen determination, the amount of oxygen less than 25% of original content could not be quantitatively measured. The negative correlation between volatile compounds formation and oxygen content suggests that the volatile compounds are formed by the reaction between oil and oxygen, as was expected[8].

The peaks of oxygen (peak 2) and nitrogen (peak 3) were identified by the combination of mass spectrometry and gas chromatographic retention time(Fig. 1). The first peak appeared at the retention time of 4.4 min after 1 day of storage, and the amount increased as the storage time increased. The compound of peak 1 was found to have the exactly same retention time of hydrogen. To identify the peak 1 compound again, Molecular Sieve 13X column(6′×1/8″ OD) and Chromosorb 102 column(16′×11/8″ OD) were also used. The compound of peak 1 appeared at the same retention time of hydrogen from both columns. However, we could not identify the compound by Mass Spectra due to very low molecular weight. Based on the results of gas chromatography and mass spectrometry, peak 1 was positively identified as hydrogen. The similar gas chomatograms of molecular hydrogen were also obtained from the samples of DF palm olein and rice bran oil.

Hydrogen content in the headspace of oil samples during storage are given in Table 1. It is well known that the molecular hydrogen is released from fatty carboxyl group in the initiation step of lipid autoxidation which results in free fatty radical[8]. Subsequently, the peroxy radical abstracts a hydrogen from another unsaturated fat molecule in the propagation step. The hydrogen

Table 1. Effect of storage time on the contents of volatile compounds(V), oxygen(O) and hydrogen(H) in headspace of rice bran oil, double fractionated(DF) palm olein, and soybean oil

Storage time (days)	Rice bran oil			DF palm olein			Soybean oil		
	V* $\times10^3$	O* $\times10^3$	H*	V $\times10^3$	O $\times10^3$	H	V $\times10^3$	O $\times10^3$	H
0	27	174	0	27	174	0	27	174	0
4	43	133	1178	28	152	487	53	113	934
8	77	50	4719	33	121	1217	145	46	7326
12	131	46	8647	52	77	2737	291	46	14257
16	350	45	12027	77	51	5625	733	46	20458
20	530	45	15570	181	51	10570	1019	46	26490

* Expressed in electronic counts

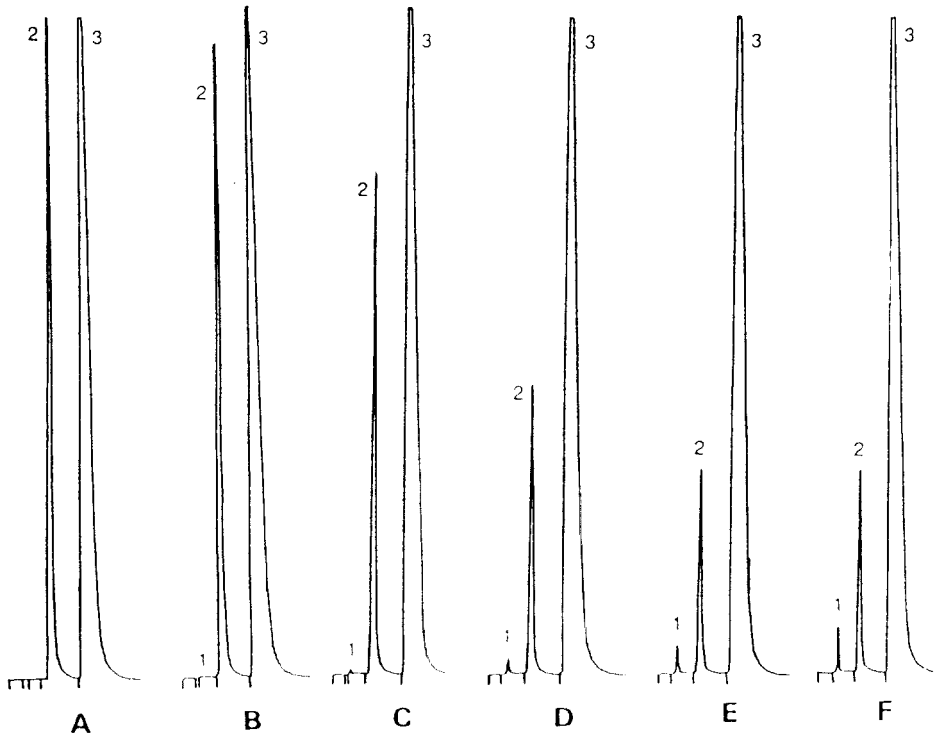

Fig. 1. Gas chromatograms of molecular oxygen in headspace of soybean oil during storage. Peak 1, Hydrogen; 2, Oxygen; 3, Nitrogen. A, 0; B, 2; C, 4; D, 6; E, 8 and F, 10 days storage.

content in the headspace appeared less than volatile compounds content since hydrogen is released from fat molecule only in the initiation stage.

Since the volatile compounds content and hydrogen content in the headspace increased, and the oxygen content decreased as the storage time increased, the linear regression equation was developed between the contents of volatile compounds, hydrogen and oxygen in the headspace. The high positive correlation coefficients ($r > 0.95$) between volatile compounds content and hydrogen content were observed with all samples tested(Table 2). The correlation coefficients between volatile compounds and oxygen contents, and between hydrogen and oxygen contents were found to be in the range of $-0.61 \sim -0.84$.

With the results of the study, it is proposed that single anlaysis of hydrogen and oxygen in headspace of oil using gas chromatography can be used instead of separate determination of volatile compounds and oxygen, which have widly been used for determination of flavor stability of oils.

Table 2. Correlations between analytical values of rice bran oil, DF palm olein and soybean oil*

	Rice bran oil		DF palm olein		Soybean oil	
	V	O	V	O	V	O
O	-0.612	-	-0.732	-	-0.608	-
H	0.951	-0.818	0.979	-0.842	0.963	-0.762

* Legends are the same as in Table 1.

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(Received Oct. 28, 1988)

가스크로마토그래피에 의한 식용유의 향미 안정성 측정

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식용유의 향미 안정성을 측정하기 위하여 가스크로마토그래피를 이용하여 유지시료의 윗 공간내에 있는 총 휘발성물질, 산소 및 수소의 양을 측정하였다. 유지의 산패가 진행됨에 따라 총 휘발성물질의 양과 수소의 양은 유의적으로 증가하였으며, 두 값 사이의 상관계수는 0.95 이상으로 높게 나타났다. 이러한 상관관계는 유지의 향미 안정성을 측정하기 위하여 가스크로마토그래피를 반복하여 실험할 필요없이 시료 윗 공간내의 수소와 산소의 양을 한 칼럼을 사용하여 동시에 측정함으로써 유지의 향미 안정성을 나타내는 지표로써 수소와 산소의 함량이 사용될 수 있음을 시사하였다.