Evaluation of Oxidation of Vegetable Oils by Pyrolytic Sulfurization Gas Chromatography

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Synopsis. Oxygen determination by pyrolytic sulfurization gas chromatography[1-5] was applied to observe the degree of oxidation of vegetable oils. Oxidation deterioration of vegetable oil and the effect of antioxidants were evaluated.

Elemental analysis by use of pyrolytic sulfurization gas chromatography (PSGC), adopting the sulfur combustion method instead of the conventional oxygen combustion, has its prime feature in its ability to determine the oxygen content of a sample together with the contents of other constituent elements. This report deals with a study on the oxidation of vegetable oils performed as an application of this advantageous oxygen determination by PSGC. Both the oxidation deterioration of vegetable oils and the effect of antioxidants on it were investigated.

Experimental

Reagents. The sulfur used as a reaction agent together with a sample was obtained by purifying[6] commercially available sulfur (chemically pure) by the Bacon-Fanelli method. Drying oils (linseed, and soybean oils), a semidrying oil (sesame oil) and nondrying oils (olive, and castor oils) as the sample oils were obtained commercially. The aromatic antioxidants (*t*-butylhydroquinone, propyl gallate, and hydroquinone) were of JIS special grade quality.

Apparatus. A sampler, a displacement apparatus and an electric furnace were used. Gas chromatograms were taken on a Shimadzu GC-4B gas chromatograph.

Procedure. The oxidation test of the vegetable oils was made as follows: A sample oil (25 ml) was introduced into a 50 ml round-bottom flask, and oxidized by bubbling oxygen gas into it at a flow rate of 180 ml min^{-1} under agitation at 1400 rpm. At fixed time intervals after the start of the reaction, specimens (about 0.5 mg) were taken out and subjected to elemental analysis by PSGC. The measurements were made at different temperatures between 50 and 150 °C. Each type of drying, semidrying, and nondrying oils was used as the sample vegetable oil.

For the examination of the effect of antioxidants, sample oils containing 8.2×10^{-4} mol l^{-1} of antioxidants were used, and analysis by PSGC was made in the same way as for the oxidation test described above. The antioxidants used were aromatics.

The analytical conditions of PSGC were as follows: About 0.5 mg of a vegetable oil and 5 mg of sulfur were sampled into an ampoule, and allowed to react at a high temperature under a pressurized helium atmosphere. The reaction products were subjected to gas chromatography under the following conditions: Porapak QS 150 cm×4ϕ Teflon, Chromosorb 104 50 cm×4ϕ Teflon; column temperature 85 °C; carrier gas He 50 ml min^{-1}; and detector TCD.

Results and Discussion

Fats and oils generally consist of glycerides, which are susceptible to oxidation when they are of unsaturated types. Most of vegetable oils, in particular, strongly tend to be oxidized because of their being unsaturated glycerides.

Under the conditions adopted, the pyrolytic sulfurization products from vegetable oils were limited to three species (H_2S, COS, CS_2) regardless of the kinds of vegetable oil:

$$\text{Vegetable oil (C, H, O)} \xrightarrow[\text{Sulfur}]{950\,^\circ\text{C}} [H_2S, COS, CS_2]$$

where carbon contained in the sample was converted to carbonyl sulfide (COS) and carbon disulfide (CS_2); hydrogen to hydrogen sulfide (H_2S); and oxygen wholly to carbonyl sulfide (COS). Figure 1 shows the oxidation curves derived from the pyrograms, at an oxidation temperature of 100 °C, of typical vegetable oils. According to this figure, castor oil and sesame oil underwent no change under the conditions adopted for oxidation, conceivably because castor oil consists primarily of the triglyceride of hard-to-oxidize ricinoleic acid and sesame oil is accompanied by natural antioxidants. Elemental analysis data by PSGC of vegetable oils are shown in Table 1.

Figure 2 shows the oxidation curves for soybean oil

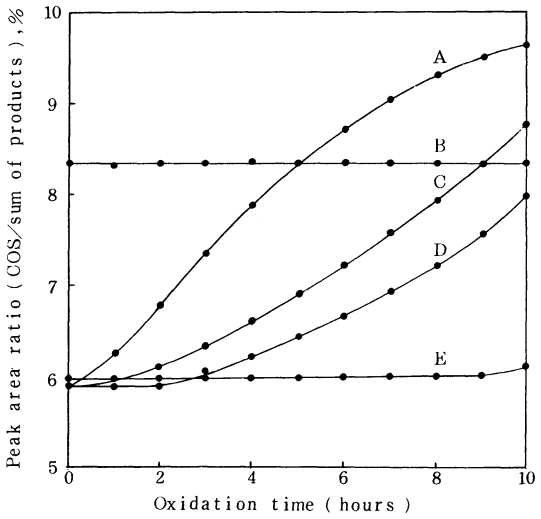

Fig. 1. Oxidation curves of vegetable oils.
Reaction temperature: 100 °C. A: linseed oil, B: castor oil, C: soybean oil, D: olive oil, and E: sesame oil.

Table 1. Analytical Results of Vegetable Oils

Sample	Oxidation time /h	Found (%)		
		C	H	O
Linseed oil	0	78.73	10.96	10.31
	10	73.81	10.17	16.02
Soybean oil	0	78.20	11.19	10.61
	10	74.15	10.90	14.95
Sesame oil	0	77.97	11.37	10.66
	10	77.78	11.43	10.79
Olive oil	0	78.07	11.43	10.50
	10	74.97	11.29	13.77
Castor oil	0	74.09	11.50	14.41
	10	74.60	11.08	14.32

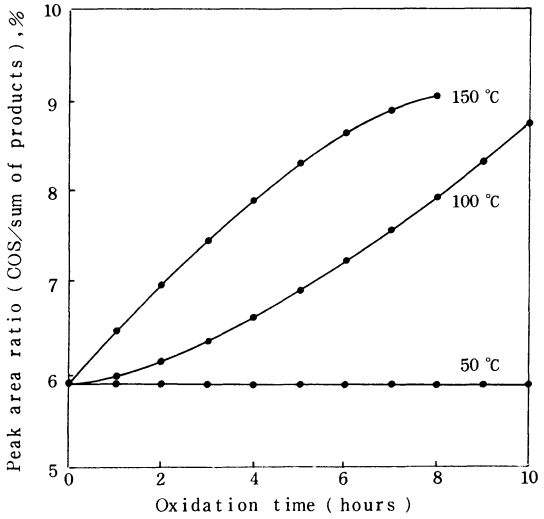

Fig. 2. Oxidation curves of soybean oil.

at varied oxidation temperatures of 50 °C, 100 °C, and 150 °C. As can be seen from this figure, oxidation of vegetable oils is markedly accelerated by the rise of temperature as with general chemical reactions.

The effect of antioxidants on the oxidation of vegetable oils was also investigated. Figure 3 shows the effects of antioxidants on the oxidation rate of soybean oil. The oxidation temperature was 100 °C and the concentration of each antioxidant was 8.24×10^{-4} mol l^{-1}. The same procedure may be applied to other vegetable oils. Figure 4 shows the effect of the concentration of the antioxidant (*t*-butylhydroquinone) on the induction period for soybean oil. The oxidation temperature was 100 °C. Figure 4 indicates that the induction period reaches a maximum when the concentration of *t*-butylhydroquinone is approximately 150 ppm. This procedure may be applied to other antioxidants.

One of the known methods for examining the degree of oxidation of a fat or an oil comprises measuring the weight gain caused by a reaction between the sample fat or oil and oxygen. The data obtained by this method agree well with the analytical data determined by PSGC.

The coefficient of variation in the peak area ratio of each sample vegetable oil calculated by effecting the

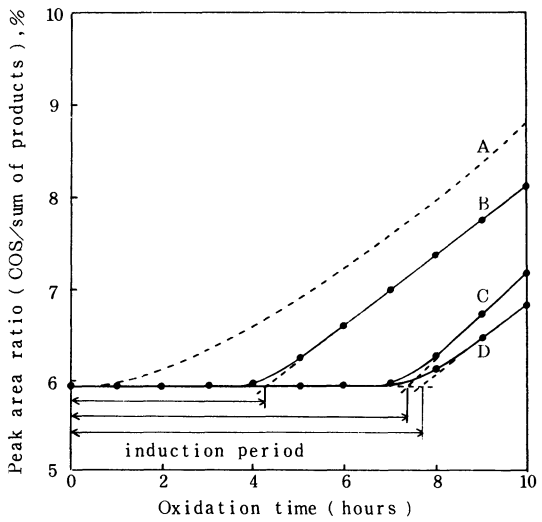

Fig. 3. Effect of antioxidants on the rate of oxidation of soybean oil.
Reaction temperature: 100 °C, and antioxidant concentration: 8.24×10^{-4} mol l^{-1}. A: oil alone, B: oil plus *t*-butylhydroquinone, C: oil plus propyl gallate, and D: oil plus hydroquinone.

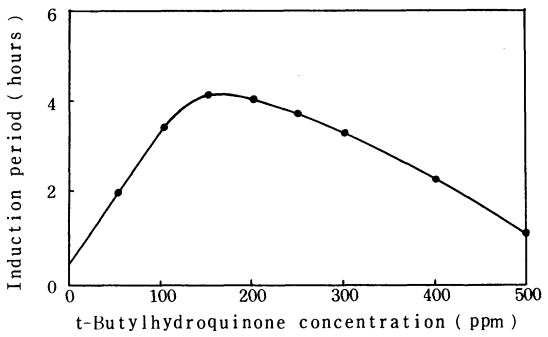

Fig. 4. Relationship between induction period and *t*-butylhydroquinone concentration for soybean oil.
Reaction temperature: 100 °C.

determination by PSGC six times did not exceed 0.5%. In view of this coefficient value, the method of this study can be considered fully suitable for oxidation tests on vegetable oils.

From the findings described above, this method can be considered useful in estimating the oxidation deterioration of vegetable oils and the effect of antioxidants on it. It can also be useful for food analyses and food control of fats and oils, because most of the vegetable oils for home use consist primarily of unsaturated glycerides susceptible to oxidation.

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