Rapid Determination of Residual Hexane in Oils by Gas Chromatography Using Pyrolyzer

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ABSTRACT AND SUMMARY

A simple, direct gas chromatographic (GC) technique is described for the quantitative determination of residual hexane in extracted vegetable oils. The method is rapid and sensitive to one ppm hexane. A platinum boat, on which sample oil was placed, is inserted into a pyrolysis chamber in a pyrolyzer attached to a GC, and heated at 150 C for 60 sec to carry the evaporated hexane into the GC with a carrier gas. In the method, the column of GC may be used without the possibility of contamination because the sample is not injected directly into the GC. The method should be useful for the quality control of solvent extracted oil products.

INTRODUCTION

In Japan, only hexane is now permitted as an extracting solvent for edible oils by Food Hygiene Laws. These laws state that the solvent should not be detected in final oil products. The three methods of determining residual hexane in extracted vegetable oils are: head space gas analysis method (1), solvent extraction method (2-4), and direct gas chromatographic (GC) method (5-7). The head space gas method and the extraction method are not suitable for a quantitative determination because of the inferior sensitivity. The direct GC method is an excellent method but has a problem of column contamination which is very troublesome when many samples are so analysed. Recently Dupuy et al. (8,9) reported that good results were obtained by direct GC method using an inlet liner. This paper presents a simple, rapid method to determine the residual hexane in vegetable oils by connecting the GC with a pyrolyzer used for analyzing usual high polymers.

EXPERIMENTAL PROCEDURES

Materials

Hexane extracted crude, neutralized, bleached, winterized, and deodorized cottonseed and soybean (not winterized) oils, and hexane free cottonseed oil (experimentally prepared from screwpress oil) were furnished by Sumit Seiyu Co., Ltd., Chiba, Japan, and Nisshin Seiyu Co., Ltd., Yokohama, Japan.

Procedure

About 20 mg of oil was accurately weighed on a platinum boat, and the boat was inserted in a pyrolysis chamber of a Shimazu pyrolyzer PYR-1A attached to a Shimazu GC-5A gas chromatograph with a flame ionization detector, a R-101 recordor, and a 1A integrator. After heating at 150 C for 60 sec, the selecting cock of the pyrolyzer was positioned and after 10 sec the platinum boat was drawn up to the beaters. Volatile matters carried into the GC passed through a column and were detected in the flame ionization detector.

GC condition was as follows: column, 1.5 m long x 4 mm outside diameter, U-type stainless steel, packed with Porapack P (Waters Associates, Framingham, MA), 80-100 mesh; carrier gas, nitrogen 40 ml/min; hydrogen 35 ml/min; air, 0.8 l/min; detector temperature, 200 C; column temperature, 140 C. The condition of pyrolyzer was as follows: pyrolysis chamber temperature, 150 C; heating time 60 sec; pyrolyzer carrier pipe temperature 150 C; selecting cock temperature, 150 C.

Preparation of Calibration Curve

One g of n-hexane (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was added into 99 g hexane free cottonseed salad oil (10,000 ppm). This oil was diluted to prepare standard oils containing 250, 100, 50, 10, 5, and 1 ppm n-hexane. Each 20 mg of these oils was accurately weighed and inserted into the pyrolysis chamber, and the calibration curve was prepared according to the abovementioned procedure.

Determination of Heating Time and Heating Temperature in Pyrolysis Chamber

The temperature in the pyrolysis chamber was adjusted to 150 C, and 20 mg of the standard oil containing 5 ppm n-hexane placed on the platinum boat was heated for 10, 20, 30, 40, 50, 60, 80, and 100 sec to determine a suitable heating time. Each 20 mg of the standard oils containing 5 ppm and 1 ppm n-hexane was heated at 100, 150, 200, and 250 C for 60 sec to determine a suitable heating temperature in the pyrolysis chamber.

TABLE I

Determination of Residual Hexane in Vegetable Oils from Different Stage

Type of oil	Stage	Hexane determined (ppm)	Methylcyclopentane[a] determined (ppm)
Cottonseed	Crude	110	115
	Neutralized	80	80
	Bleached	19	22
	Winterized	12	13
	Deodorized	ND[b]	ND
Soybean	Crude	310	320
	Neutralized	88	110
	Bleached	3	5
	Deodorized	ND	ND

[a]Methylcyclopentane was an impurity in hexane used in oil refineries.

[b]ND = none detectable.

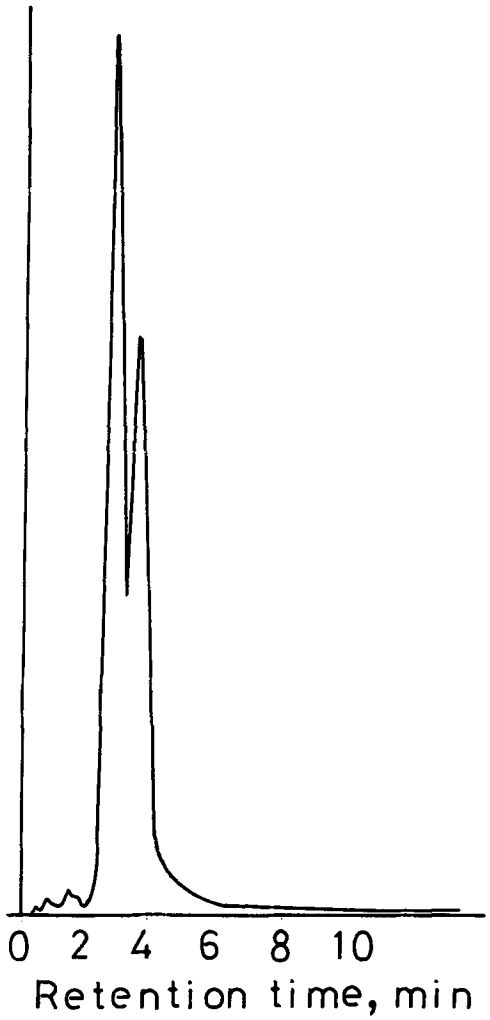

FIG. 1. Gas chromatogram of cottonseed crude oil extracted with hexane.

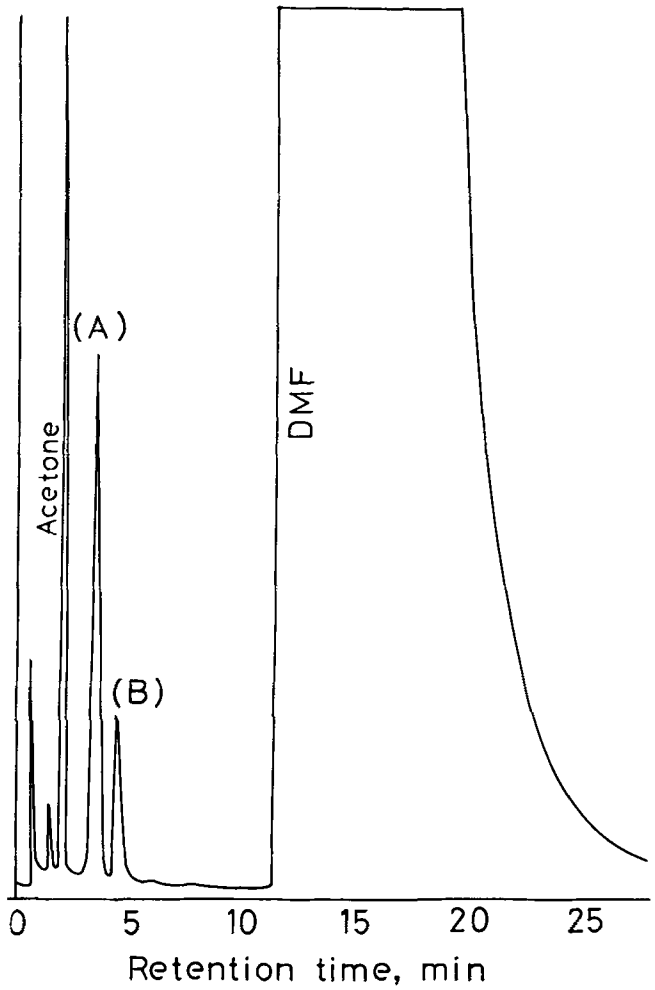

FIG. 2. Gas chromatogram of dimethylformamide (DMF) extract from cottonseed crude oil.

Determination of Impurities in the Hexane Used in Oil Refineries

Because the hexane used for extraction in the oil refineries consisted of two components, Hitachi GC mass spectrograph (GC-MS) RMU-6MG was used for the identification of these components.

RESULTS AND DISCUSSION

Table I shows the contents of residual hexane in crude, neutralized, bleached, winterized, and deodorized cottonseed and soybean oils from two oil refineries by the method. Most residual hexane was removed in the bleaching stage. It was assumed that in this stage the residual hexane was removed by adsorption of bleaching earth and evaporation in high vacuum and high temperature. In the deodorizing stage the residual hexane was completely removed by the high temperature (260-270 C) and the high vacuum (3 mm Hg).

In the relationship between heating time in the pyrolysis chamber and the height of n-hexane peak, the n-hexane peak reached a plateau after the heating time of 50 sec and nonsolvent "oil peaks" (5) increased in proportion to the increase of heating time. So the heating time in this experiment was set up to 60 sec. In the relationship between heating temperature in the pyrolysis chamber and the height of n-hexane peak, the nonsolvent "oil peaks" did not appear at 100 C, but the peak of 1 ppm n-hexane was very low. At 200 C and 250 C, the peak of 1 ppm n-hexane

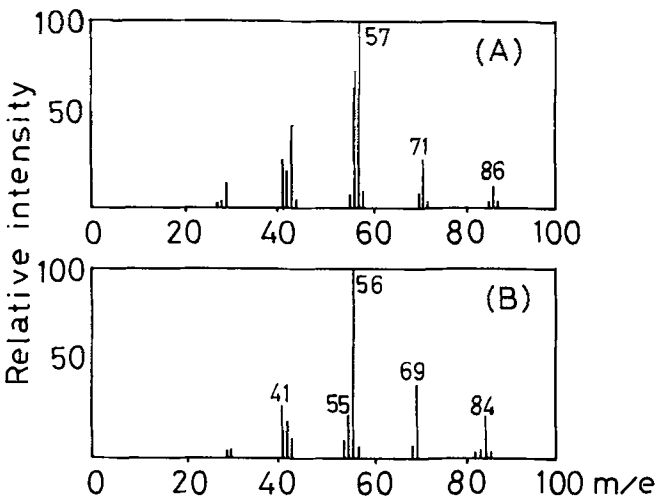

FIG. 3. Mass spectra of components identified as n-hexane (A), and methylcyclopentane (B).

appeared well, but the increase of nonsolvent "oil peaks" interfered with the determination. The temperature of the pyrolysis chamber, therefore, was set up to 150 C.

The calibration curve of n-hexane in the method was completely rectilineal. Figure 1 shows the gas chromatogram of cottonseed crude oil extracted with hexane. In Figure 1, two main peaks were observed, so the crude oil was extracted with dimethylformamide (DMF) and deter-

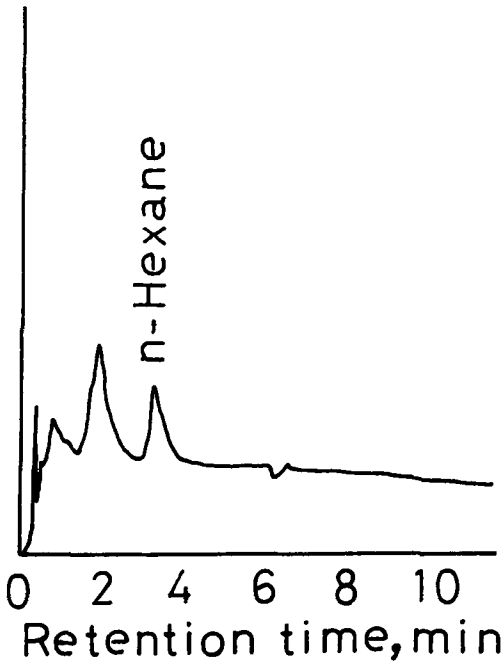

FIG. 4. Gas chromatogram of cottonseed oil containing 1 ppm n-hexane.

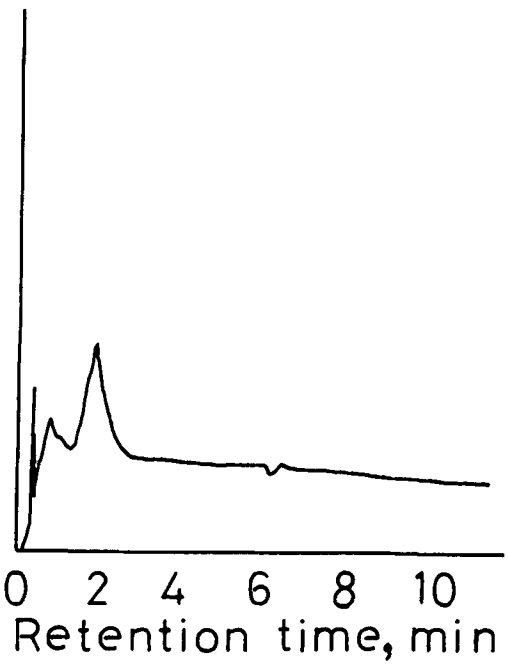

FIG. 5. Gas chromatogram of hexane free cottonseed salad oil.

mined by GC-MS to identify these substances. The gas chromatogram is shown in Figure 2 and mass spectra are shown in Figure 3. From the retention values of the chromatogram and mass spectra, it was determined that these peaks were n-hexane and methylcyclopentane, an impurity in hexane. Figure 4 shows the gas chromatogram of cottonseed oil containing 1 ppm n-hexane, and Figure 5 shows that of hexane-free cottonseed oil. From these figures it was recognized that 1 ppm residual hexane can be well detected by the method.

The method seemed to be useful for the rapid determination of residual hexane in vegetable oils and may be applied as a mean of quality control in oil refineries.

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