Rapid Quantitative Determination of Residual Hexane in Oils by Direct Gas Chromatography[1]

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ABSTRACT

A simple, direct, gas chromatographic technique is described for the quantitative determination of residual hexane in extracted vegetable oils. The method if rapid and sensitive to one ppm hexane. The inlet liner of a gas chromatograph was packed with 1½ in. glass wool, and 25 mg oil was added onto it. The sample was capped with a small plug of glass wool, and the liner was inserted in the heated inlet of the gas chromatograph. Residual hexane rapidly eluted onto the Poropak P column by heat, and carrier gas was resolved in 20 min by temperature programing between 70-180 C. The method appears useful for monitoring continuous solvent removal processes.

INTRODUCTION

Essentially all of the vegetable fats and oils produced in the U.S. today are extracted by hexane. Because it is flammable, nearly all of the hexane must be removed from such products before they can be refined safely. Residual hexane in vegetable fats and oils has been determined in different ways. The flash point procedure (1) has been used extensively, but the method is not quantitative and probably would not detect hexane below 300 ppm. The gas chromatographic procedure (2), quantitative and sensitive to 100 ppm residual hexane in crude oils, is somewhat complex. The sample must be injected into a precolumn which must be changed periodically to avoid contamination problems. Pardum and Vogel (3) determined hexane in extracted vegetable oils by blowing room temperature air through the sample and passing the hexane-laden air through a Dräger indicator tube. Although the method is rapid and only moderately complex, the limit of detection is ca. 100 ppm. Quantitation of hexane in oils to 20 ppm is possible by the procedure of Watts and Holswade (4). However, because the oil is injected directly onto the chromatographic column, it must be removed periodically, and ca. 8 in. of the column forepacking must be replaced to preclude "tailing" of the solvent peaks.

This paper reports the development of a simple and rapid gas chromatographic procedure for determining residual hexane in extracted vegetable oils to a level of 1 ppm.

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EXPERIMENTAL PROCEDURES

Materials

Porapak P (a porous polymer) came from Waters Associates, Framingham, Mass.; silicone O-rings (heated at 200 C for 2 hr to remove volatile impurities) were obtained from Applied Science Laboratories, College Station, Pa.; Pyrex glass wool (heated at 200 C for 16 hr to remove volatiles) came from Corning Glass Works, Corning, N.Y.; and commercial crude peanut oil, commercial cottonseed, and soybean oils (crude, refined, and deodorized) were used.

Chromatographic Conditions

Instruments used included a MicroTek 2000 MF gas chromatograph with dual independent hydrogen flame detectors, a Westronics LD 11B recorder, and an Infotronics CRS-100 integrator. The column was ¼ in. outside diameter stainless steel U-tubes, 2 ft long, packed with Porapak P. Flow rates were helium carrier gas (60 ml/min through each column), hydrogen (52 ml/min to each flame), air (1.2 ft^3/hr [fuel and scavenger gas for both flames]). The temperature was inlet at 110 C, detector at 200 C, column oven programed at 5 C/min for 22 min between 70-180 C, initial hold at 70 C for 2 min, and final hold at 180 C for ca. 10 min or until column was clean. Attenuation was 10 x 1 for

TABLE I

Determination of Residual Hexane in Vegetable Oils by Direct Gas Chromatography

Sample no.	Type of oil[a]	Flash point F	Hexane determined (ppm)
1	Crude soybean	180	3500
2	Crude soybean	210	1600
3	Crude soybean	250	1000
4	Crude soybean	250	1000
5	Crude soybean	320	550
6	Refined soybean		170
7	Refined soybean		150
8	Crude cottonseed		5000
9	Crude cottonseed		950
10	Crude cottonseed		450
11	Crude cottonseed		200
12	Crude cottonseed		40
13	Crude cottonseed		35
14	Crude, screwpress cottonseed		ND[b]
15	Refined cottonseed		80
16	Refined cottonseed		50
17	Refined cottonseed		6
18	Refined cottonseed		5
19	Crude peanut		20

[a]Hexane extracted with exception of sample 14.
[b]ND = none detectable.

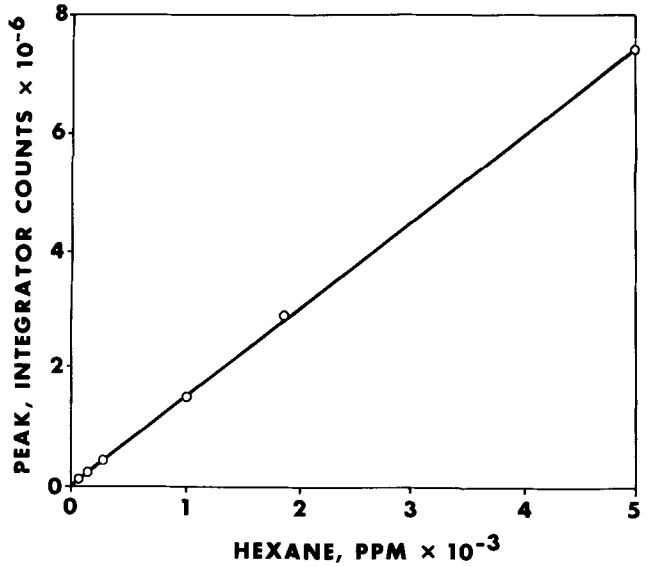

FIG. 1. Direct gas chromatograph calibration plot for converting peak areas to ppm of hexane.

electrometer, auto x 1 for integrator; chart speed was 30 in./hr. A silicone O-ring was positioned around the ¼ in. column which projected into the bottom of the inlet of the gas chromatograph, thus forming a seal with the lower lip of the liner and the base of the inlet.

Sample Preparation and Analysis

The lower half of a 3 3/8 in. x 3/8 in. outside diameter borosilicate glass tubing (inlet liner) was packed with glass wool. A 25 mg sample of vegetable oil was added onto it and covered with a small plug of glass wool. The septum nut, septum, and retainer nut of the gas chromatograph were removed, and the liner with sample was inserted in the inlet of the gas chromatograph. A silicone O-ring sealed the base of the inlet and the lower lip of the liner as the retainer nut was tightened against the upper lip of the liner. When the inlet system was closed with the septum and septum nut, the carrier gas was forced to flow upward and then down through the sample. A detailed illustration of this type assembly has been presented (5). The integrator and programer were turned on immediately. Residual hexane was eluted rapidly from the oil onto the column by the heat and carrier gas. The column, temperature programed between 70-180 C, then resolved the hexane isomers from other volatile components in the oil.

Standardization

A calibration curve for 25 mg vegetable oils was prepared as follows. A stock solution of cottonseed oil containing 500 ppm hexane was prepared by adding 22.5 mg (34 μliter) hexane (density 0.66) to 45 g hexane-free oil. Aliquots of 0.5, 5, 10, 50, 100, and 250 mg were analyzed by the direct gas chromatographic procedure described. Since each aliquot of stock-solution contained the same amount of hexane as a 25 mg sample of vegetable oil having 10, 100, 200, 1000, 2000, or 5000 ppm residual hexane, a calibration curve was constructed as shown in Figure 1 for converting peak area to ppm of hexane.

RESULTS AND DISCUSSION

Residual hexane was eluted rapidly from vegetable oils by the additive effect of heat, carrier gas, and increased sample surface area.

Data of residual hexane for six types of vegetable oils are shown in Table I. Samples 1-5 were crude commercial soybean oils whose flash points were furnished by the processors. The flash points of these samples were related inversely to their hexane contents. Figure 2 is a typical gas chromatograph curve for a crude soybean oil (sample 4) containing 1000 ppm residual hexane. The magnitude of the isomer peaks is evident by the attenuation. Crude and refined oils were analyzed by the same procedure.

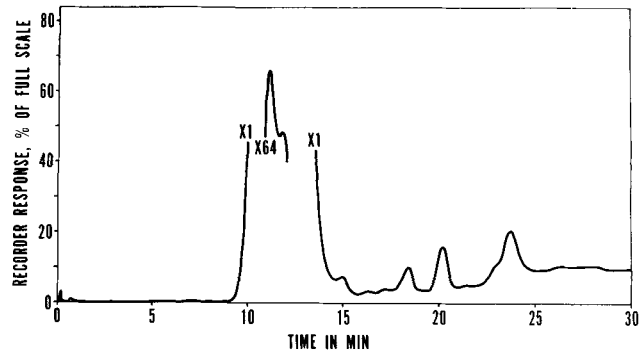

FIG. 2. Representative gas chromatograph curve of crude soybean oil containing 1000 ppm residual hexane.

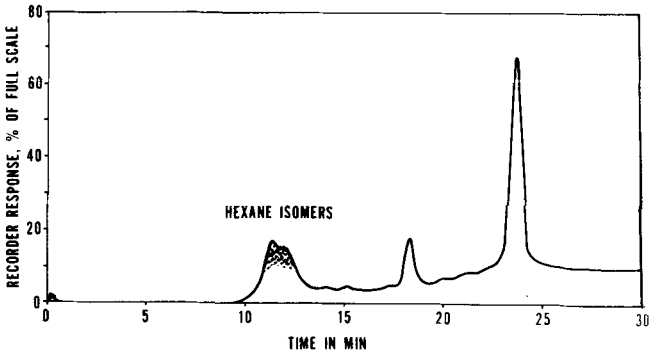

FIG. 3. Representative gas chromatograph curve of refined cottonseed oil containing 5 ppm residual hexane.

The versatility of this direct gas chromatograph method is shown by the analyses of samples 8-13. The residual hexane in these crude cottonseed oils varied from 35-5000 ppm; yet the operating procedure was the same.

No residual hexane was found in sample 14, which was a crude, screwpress cottonseed oil.

The analyses of refined cottonseed oil samples 15-18, which contained low levels of hexane, demonstrated the sensitivity of this direct gas chromatograph method of analysis. Figure 3 is the gas chromatograph curve of sample 18 which contained 5 ppm residual hexane. The peak sizes of the hexane isomers indicated that 1 ppm hexane in oils can be detected.

Although this study was limited to detection of residual hexane in oils, the technique, with appropriate gas chromatographic adjustments, also may be used to detect other volatile solvents in vegetable oils. Such solvents as acetone or isopropyl alcohol should be detectable by this method by varying the temperature program, carrier gas flow rate, or adsorbent.

A simple and direct gas chromatograph procedure was developed to determine residual hexane in extracted vegetable oils. The method is rapid, sensitive to 1 ppm hexane, and unique in that the sample was not injected onto the column. Countless samples could be analyzed without a column change.

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