A Rapid Procedure for the Determination of Residual Hexane in Oilseed Meals and Flours[1]

SARA P. FORE and **H.P. DUPUY**, Southern Regional Research Laboratory, New Orleans, Louisiana 70179[2]

ABSTRACT

A rapid and direct gas chromatographic procedure is described for the quantitative determination of residual hexane in finely ground oilseed meals and flours. A 0.04 g sample of meal or flour is added between two small plugs of glass wool in a liner of the injection port of a gas chromatograph. The liner with the sample is placed in the heated injection port and firmly secured, and 80 µl of water is immediately injected just above the glass wool which covers the sample. Volatiles which are rapidly eluted from the sample are then analyzed by temperature-programmed gas chromatography on a 2 ft x 1/4 in. Porapak P column. The results are comparable to the results obtained by the simple and efficient but more time consuming volatilization procedure. Since results are obtained within 20 min, this rapid procedure is very useful in monitoring desolventization processes.

INTRODUCTION

A number of procedures have been developed for the determination of residual solvent in oilseed meals and flours, but none of them are rapid or sensitive enough to monitor a desolventization process in the preparation of oilseed flours. The flash-cup method (1) is time consuming and not effective below a concentration of 300 ppm of residual hexane. The azeotropic distillation procedure is very sensitive, but it involves a lot of work and the use of a correction factor which has a tendency to vary with different types of samples (2,3). The volatilization procedure is very simple and sensitive, but it takes up to 2 hr to volatilize the residual hexane in oilseed meals and flours prior to gas chromatographic analysis of the headspace gas (3).

This paper reports the development of a rapid and direct gas chromatographic (GC) procedure for the quantitative determination of residual hexane in finely ground oilseed meals and flours.

[1]Presented at AOCS Meeting, Houston, May 1971.

[2]S. Market. and Nutr. Res. Div., ARS, USDA.

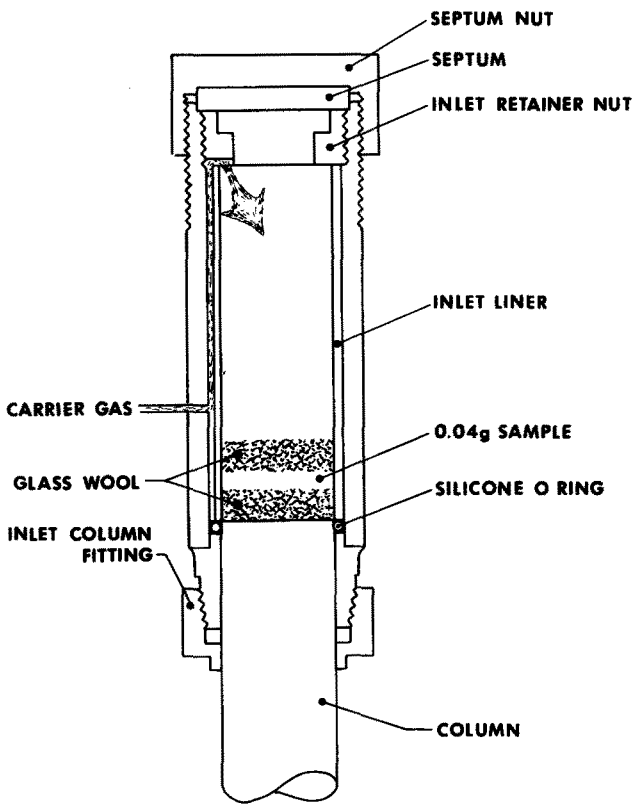

FIG. 1. Cross section of gas chromatograph inlet with inlet liner containing sample.

EXPERIMENTAL PROCEDURES

Materials

Porapak P, 80-100 mesh, was obtained from Waters Associates, Inc., Framingham, Mass. Serum bottles, red rubber septums, aluminum retainer rings and a crimper for applying the rings were obtained from Wheaton Glass Company, Millville, N.J. Neoprene serum bottle septums were obtained from Pierce Chemical Company, Rockford, Ill.

Silicone-O-rings were obtained from Applied Science Laboratories, Inc., College Station, Pa. Pyrex brand glass wool was obtained from Corning Glass Works, Corning, N.Y. The commercial cottonseed and soybean meals and flours were obtained from two commercial sources.

Rapid Elution

A small plug of glass wool was placed in the end of the liner (a 3-5/16 in. length of 3/8 in. ID borosilicate glass tubing) of the injection port of the gas chromatograph. The glass wool was tamped down lightly, and 0.04 g of finely ground oilseed meal or flour was added on top of it. The sample was capped with another small plug of glass wool. The liner with the sample was inserted on top of the

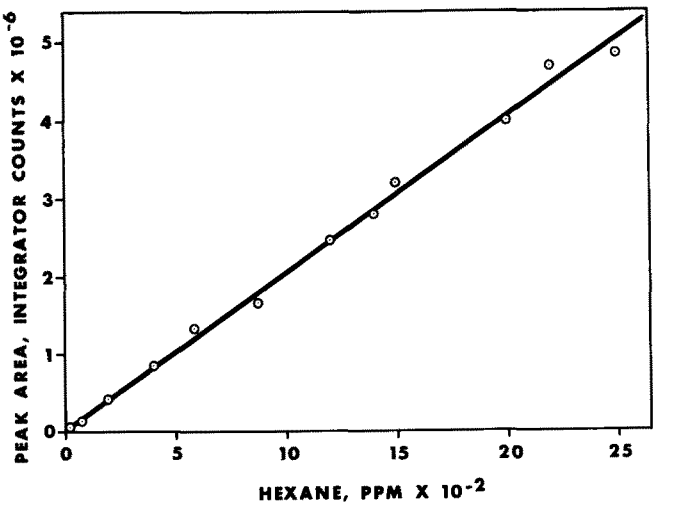

FIG. 2. Calibration curve for converting peak area expressed as integrator counts x 10^{-6} to ppm of hexane.

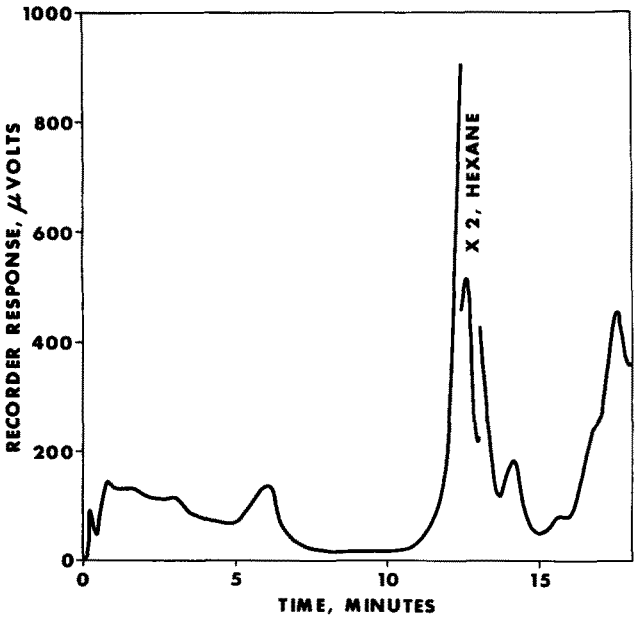

FIG. 3. Representative curve for cottonseed flour containing about 30 ppm of residual hexane.

silicone-O-ring in the injection port of the gas chromatograph, and the inlet retainer nut was tightened firmly to form a seal between the base of the inlet liner and the injection port, thus forcing the carrier gas to flow upward and into the liner. After the septum was placed in position and tightened with the septum nut, 80 μl of water was immediately injected above the sample with a 100 μl syringe equipped with a 2 in. needle. The digital integrator and the temperature programmer were turned on. After the hexane peak had been completely eluted, the spent sample was removed from the inlet, and 20 μl of water was injected to clean the column.

Gas Chromatography (GC)

The following GC conditions were employed for rapid elution of residual hexane from finely ground oilseed meals and flours and resolution of the hexane peak. Instrument: MicroTek 2000 MF with dual independent hydrogen flame detectors. Recorder: Westronics LD 11 B. Integrator: Infotronics CRS-100. Columns: 1/4 in. OD stainless steel U-tubes, 2 ft Porapak P (80-100 mesh). Carrier gas: helium. Flow rates: helium, 70 ml/min in each column; hydrogen, 60 ml/min to each flame; air, 1.2 cu ft/hr (fuel and scavenger gas for both flames). Temperature: detector at 200 C; injection port at 105 C; columns programmed between 70 and 180 C; initial hold at 70 C for 6 min; programmed at 10 C/min for 11 min; final hold at 180 C for 4 min. Attenuation: 10 x 2 for both electrometers, Auto x 1 for integrator. Sample size: 0.04 g. Chart speed: 30 in./hr.

A silicone-O-ring (previously conditioned at 200 C for 2 hr) was inserted at the base of the injection port around the head of the column which protruded slightly into the injection port as shown in Figure 1 to form a seal between the base of the liner and the injection port.

Standardization

A calibration curve for use with a 0.04 g sample of finely ground oilseed meal or flour was prepared as follows: Equal amounts of hexane (7.3 μl, 4.8 mg) were injected into three empty 120 ml serum bottles sealed with neoprene septums and aluminum retainer rings. Thus each μl of headspace gas in the bottles contained 0.04 μg of hexane which corresponds to 1 ppm for a 0.04 g sample of meal or flour. A 0.04 g sample of hexane-free cottonseed flour was placed between two small glass wool plugs in the liner of the injection port of the gas chromatograph. The liner with the sample was inserted in the heated injection port and properly secured. An aliquot of the headspace gas from the serum bottles was withdrawn and injected above the sample of flour and followed by 80 μl of water. The integrator and temperature programmer were turned on to complete the chromatographic cycle. Several aliquots of headspace gas from each of the bottles were analyzed by this procedure as follows: Aliquots of 10, 400, 1500 and 2200 μl were withdrawn from bottle 1 and analyzed. Aliquots of 80, 880, 1400 and 2000 μl were withdrawn from bottle 2 and analyzed. Aliquots of 200, 600, 1200 and 2500 μl were withdrawn from bottle 3 and analyzed. Since each μl of headspace gas corresponds to 1 ppm of hexane for a 0.04 g sample of meal or flour, the calibration curve was easily constructed by plotting the integrator counts (peak area) against μl of headspace gas (ppm). The calibration curve is shown in Figure 2.

Since a well defined peak with an area count of about 2000 could be obtained without difficulty, the rapid and direct GC procedure should be effective for determining residual hexane down to a level of 1 ppm.

TABLE I

Determination of Residual Hexane
by Volatilization and Rapid Elution Procedures

	Hexane recovered, ppm		
		Rapid elution	
Type of sample[a]	Volatilization	Sample + water	Sample alone
Cottonseed flour	11	12	ND[b]
Cottonseed flour	30	33	ND
Cottonseed meal	11	12	ND
Cottonseed meal	135	130	5
Cottonseed meal	920	920	15
Cottonseed meal	2300	2600	25
Peanut meal	17	20	ND
Peanut meal	ND	ND	ND
Cottonseed meal	ND	ND	ND
Soybean flour	13	15	ND
Soybean flour	75	75	2
Soybean flour	125	125	2

[a]The first eight samples were prepared in the laboratory or pilot plant; the other four were commercial.

[b]None detectable.

RESULTS AND DISCUSSION

To achieve rapid and maximum elution of residual hexane from finely ground oilseed meals and flours by direct GC, it was necessary to force the carrier gas to flow through the sample which was in the liner of the injection port. It was also necessary to inject an adequate amount of water just above the sample immediately after the liner was inserted into the properly heated injection port of the gas chromatograph.

In preliminary experiments the sample was placed between two small glass wool plugs in the inlet liner which was inserted into the heated injection port of the gas chromatograph, and then the chromatographic run was completed. Under these conditions very little hexane was eluted from the sample. When water was injected above the sample immediately after it was inserted into the injection port, the hexane was eluted rapidly. However the amount eluted varied considerably and was lower than the amount obtained by the volatilization procedure (3).

After checking the geometry of the injection port, a silicone-O-ring was inserted at the bottom of the injection port around the column which protruded slightly into the port as shown in Figure 1. The inlet liner was inserted in the injection port and tightened firmly with the septum nut. This created a seal between the lower lip of the inlet liner and the base of the injection port which forced the carrier gas to flow upward and into the inlet liner. The steaming action of water plus the flow of the carrier gas through the sample resulted in rapid and quantitative elution of the residual hexane which was swept onto the GC column. The water also promoted the elution of extraneous volatile material, but the hexane was resolved from this material by temperature programming between 70 and 180 C at 10 deg/min after an initial hold period of 6 min. A representative chromatogram obtained from a sample of cottonseed flour containing about 30 ppm hexane is shown in Figure 3.

Different size samples (0.02-0.1 g) of meal or flour were analyzed, but the best results were obtained with about 0.04 g samples. This amount could be easily weighed on a small torsion balance, and the results were highly reproducible when 75-100 μl of water was injected on top of this size sample. If only 50 μl of water was injected, the residual hexane was not eluted quantitatively. The residual hexane from the 0.02 g sample could be eluted quantitatively, but the results were less reproducible. The residual hexane from larger samples such as 0.1 g could not be eluted quantitatively. When the inlet liners with such large samples were reinserted in the injection port for a second chromatographic run, a considerable amount of residual hexane remaining from the previous run was eluted. When the spent inlet liners with a 0.02 or 0.04 g sample were reinserted in the injection port and 80 μl of water was injected over the sample, a negligible amount of residual hexane was eluted. Although reproducible and quantitative results were obtained when the injection port was heated between 105 and 140 C, the injection port was heated only to 105 C to minimize decomposition of the meal or flour.

A number of finely ground oilseed meals and flours were evaluated for residual hexane with this direct GC procedure. These consisted of laboratory samples of cottonseed meals and flours which were prepared by hexane extraction or mixed solvent (acetone-hexane-water) extraction, samples of peanut meals which were prepared by hexane extraction, and commercial samples of soybean flours which were prepared by hexane extraction. Screw-pressed meals were used as controls, and no hexane could be detected. All the samples were analyzed in duplicate by this direct GC procedure and by the volatilization procedure (3) for comparison. The variation between the duplicate analyses by each procedure was only between 0 and 9% of their averages. The results obtained by the two procedures are comparable as shown in Table I. The significant effect of water in accelerating the elution of the residual hexane is also shown in Table I.

This direct GC technique is an ideal procedure for monitoring the desolventization of oilseed meals, where rapid analysis is essential. The special techniques described, when applied by the practiced analyst, provide a very rapid and efficient procedure for determining residual hexane in finely ground oilseed meals and flours. In applications where time is not important, the simpler volatilization procedure may be preferable.

Samples covering a large range of residual hexane, approximately 1-2500 ppm, can be analyzed by either procedure.

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[Received November 8, 1971]