Determination of Residual Solvent in Oilseed Meals and Flours: II. Volatilization Procedure[1]

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Abstract

A simple volatilization procedure was developed for the determination of residual hexane in oilseed meals and flours. A 2 g sample of meal or flour and 0.2 g of water are weighed into a 120 ml serum bottle, which is sealed and heated at 110 C for 2 hr in an oven. A 1 ml aliquot of the head-space gas is then analyzed by gas chromatography. The concentration of residual hexane is easily determined by comparing the area of the appropriate peak of the chromatogram with a calibration chart. Results are reproducible within ±20%, and concentrations as low as 1 ppm can be detected. The technique is much simpler and more efficient than other procedures available. It also appears to be useful for determining other residual solvents such as acetone and isopropanol, and acetone impurities such as mesityl oxide and diacetone alcohol in oilseed meals and flours.

Introduction

To identify the factor or factors that impart off-flavors to cottonseed meals and flours prepared by extraction with a mixture of acetone, hexane and water (AHW), it was desirable to determine the concentration of residual hexane and acetone and of acetone impurities such as diacetone alcohol and mesityl oxide (1). The procedure of Black and Mustakas (2) for the determination of residual hexane in soybean flakes was investigated, but the isooctane extracting solvent did not efficiently remove residual hexane and acetone from cottonseed flours prepared by AHW extraction. Consequently, more powerful extracting solvents such as ethers, ketones and formamides were screened, and dimethylformamide (DMF) containing 5% water was found to be the most effective for removing residual solvents from oilseed meals and flours prepared by extraction with either AHW or hexane (3).

However, since it was impossible to determine whether the aqueous DMF solution completely removed the residual solvent, a second procedure was developed for comparison. This new technique, a volatilization procedure, proved to be more simple, rapid and effective than other procedures for determining residual hexane in oilseed meals and flours.

Experimental Procedures

Materials

Porapak P and Q, 80–100 mesh, were 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. More heat-resistant silicone rubber septums were tried, but they absorbed hexane upon heating and standing. Although the red rubber septums also absorbed hexane during prolonged heating at high temperature, they performed well under the conditions recommended. Plastipak disposable plastic syringes were obtained from W. H. Curtin & Co., New Orleans, La. The commercial cottonseed and soybean meals and flours were obtained from four commercial sources.

Volatilization

Two grams of oilseed meal or flour and 0.2 g of water were weighed into a 120 ml serum bottle, which was immediately sealed with a red rubber septum and an aluminum retainer ring. After the sample was heated in an oven at 110 C for 2 hr, a 1 ml aliquot of the head-space gas was removed with a plastic syringe and immediately injected into the 1 ft Poropak P column of the gas chromatograph. The digital integrator and the multilinear temperature programmer were turned on immediately. Twenty seconds later, 1 ml of the head-space gas was injected into the 6 in. Porapak Q column to help confirm the presence of hexane. The temperature programmer completed its cycle in 30 min, and the chromatograph was then ready for another aliquot of head-space gas.

Gas Chromatography

The following conditions were employed for analyzing the head-space gas. Instrument: Micro-Tek 2000 MF with dual independent hydrogen flame detectors. Recorder: Westronics LD 11 B. Integrator: Infotronics CRS-100. Columns: ¼ in. o.d. stainless steel U-tubes, a) 1 ft Porapak P (80–100 mesh), b), 6 in. Porapak Q (80–100 mesh). Carrier gas: helium. Flow rates: helium, 60 ml/min in each column; hydrogen, 52 ml/min to each flame; air, 1.2 cu ft/hr (fuel and scavenger gas for both flames). Temperature: detector at 200 C; injector port at 150 C; columns programmed between 70 and 180 C; initial hold at 70 C for 2 min; programmed at 10 C/min for 11 min; final hold at 180 C for 3 min; cool for 10 min; equilibrate for 4 min. Attenuation: 1 × 8 for both electrometers, Auto × 1 for integrator. Sample size: 1 ml of head-space gas. Chart speed: 30 in./hr.

Standardization

A calibration chart for use with a 2 g sample of oilseed meal or flour and a 1 ml aliquot of head-space gas was prepared as follows: Hexane (0.5 mg or 0.62 µl) was injected into an empty 120 ml serum bottle sealed with a red rubber septum and aluminum retainer ring. After the bottle had been heated at 110 C in an oven for an hour, aliquots (0.1 ml, 0.2 ml, 0.4 ml, 0.8 ml, 2 ml and 4 ml) of the head-space gas were injected at 10 min intervals into the Porapak P column, which was heated isothermally at 100 C. For construction of the calibration curve, these volumes were then multiplied by a factor of 250 to convert them into terms (ppm) applicable to analysis of 1 ml of head-space gas from a 2 g sample of meal or flour, and these values were plotted against the peak area counts. The calibration chart is shown in Figure 1.

Since a well defined peak with an area count of about one thousand could be obtained without difficulty, the volatilization procedure should be effective for determining residual hexane at a level of 1 ppm.

Internal Standard

The results obtained by adding water to samples of oilseed meals and flours were comparable to the

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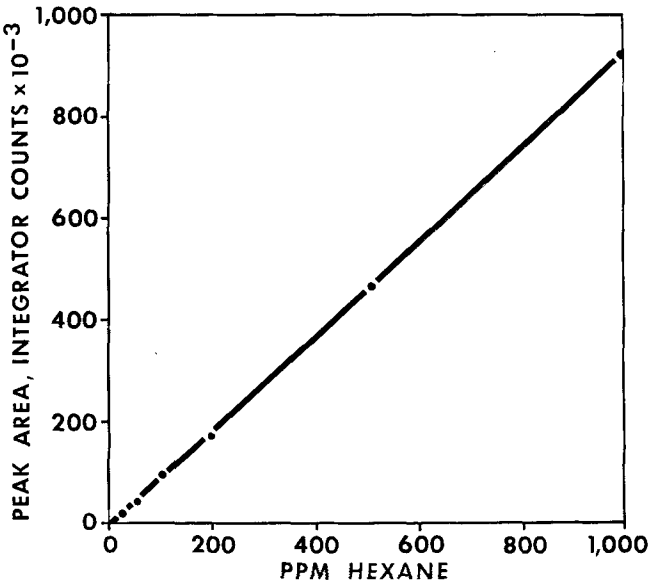

FIG. 1. Calibration chart for converting peak area count to ppm of hexane.

results obtained by adding aqueous ethanol in which ethanol was used as the internal standard.

Determination of Suitable Conditions

To achieve the maximum volatilization of residual hexane from oilseed meals and flours, the interactions among three variables, temperature, time and moisture, had to be controlled.

In preliminary studies, samples of meals and flours were heated at temperatures between 80 and 140 C. At 80 C it was impossible to obtain maximum volatilization of residual hexane and at 140 C the oilseed sample decomposed and interfered with the analysis. The results from more than a hundred analyses indicated that maximum volatilization of hexane with minimum decomposition of the oilseed sample could be achieved at about 110 C. However, even at 110 C, volatilization took much too long for practical operation. In fact, some samples required as long as 25 hr.

Then an inconsistency in results suggested a solution. Residual hexane was volatilized from 1, 2 and 3 g samples of the same meal. Instead of being equal for all samples, as expected, the apparent concentration of hexane increased as the weight of the sample increased. Interpreting this result to mean that moisture in the largest sample had facilitated volatilization, we added water before sealing the bottle. The effect of adding 10% water, a marked increase in recovery of residual hexane, is shown in Table I.

In most cases, 5% additional water was insufficient to achieve this increase, whereas 20% was no more effective than 10%.

TABLE I

Effect of Adding Water on the Volatilization of Residual Hexane

Type of sample[a]	Hexane recovered (ppm) after 2 hr at 110 C	
	Sample alone	Sample + 10% water
Soybean meal	60	130
Soybean meal	20	30
Soybean flour	130	150
Cottonseed meal	60	90
Cottonseed flour	ND[b]	ND
Cottonseed flour	40	240
Cottonseed flour	1700	2700
Cottonseed flour	430	1200

[a] The first five samples were commercial products; the other three were prepared in the laboratory or pilot plant.
[b] None detectable.

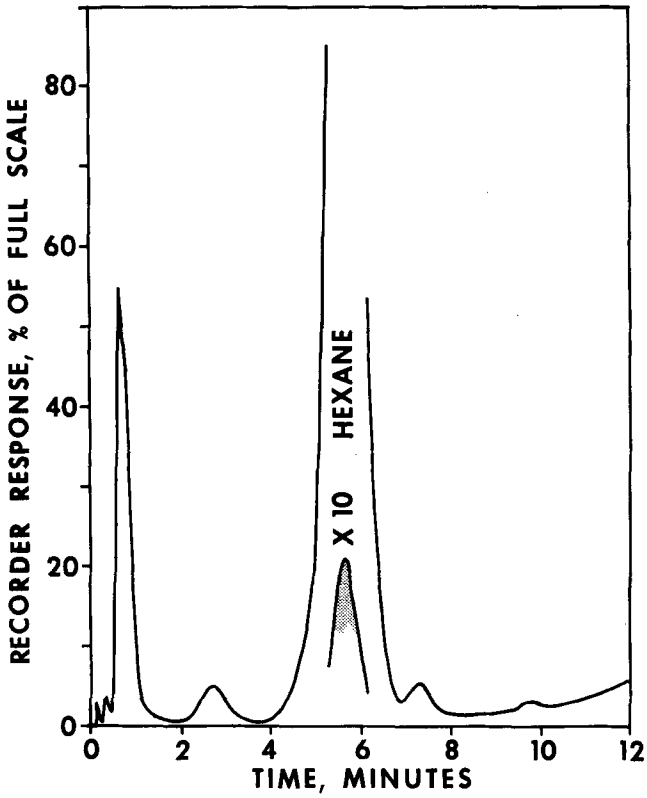

FIG. 2. Representative GC curve from a sample of oilseed meal with a residual hexane concentration of about 90 ppm.

On the basis of numerous analyses, the conditions given under Experimental Procedures were achieved; a 2 g sample with 10% additional water produced maximum volatilization of residual hexane within 2 hr. A representative curve obtained by gas chromatography is shown in Figure 2. The results were reproducible within ±20%.

Comparison With Other Methods

Recovery of Residual Hexane

Residual hexane in normally processed oilseed meals and flours is very difficult to volatilize since it is evidently strongly bound or trapped. In contrast, hexane that is simply added to the meals or flours is easily volatilized; in fact, most of it appears in the head-space gas even at room temperature. The fact that a process yields complete recovery of added hexane by no means ensures complete recovery of residual hexane.

Recovery of residual hexane by the volatilization procedure was therefore compared with determinations by three other methods: extraction with isooctane (2); extraction with DMF (3); and distillation by the Todd procedure (4) used by the Food and Drug Administration (FDA) to determine residual solvents in spice oleoresins (5). We modified the distillation method by decreasing the sample size to 25 g and increasing the amount of sodium sulfate solution to 100 ml to make it applicable to oilseed meals and flours. As shown in Table II, the volatilization procedure provided the most quantitative recovery.

FDA reports that since the distillation method recovers only 52% of hexane added to oleoresins, a correction factor must be applied to determinations of residual hexane from this material (5). However, the values shown in Table II for the distillation

method are uncorrected, because a constant correction factor cannot be applied to recovery from oilseed meals or flours. For example, using the modified Todd procedure, we recovered 65% of hexane added to a cottonseed meal prepared in the laboratory but only 38% of hexane added to a commercial cottonseed flour. Thus a different correction factor would have to be determined for each type of sample, a prohibitive requirement in applying this already tedious method to oilseed products.

Although we cannot be certain that the volatilization procedure achieves complete recovery of residual hexane, additional heating at 110 C in the presence of 10% additional moisture did not increase recovery. Moreover, when hexane was added to oilseed meals containing residual hexane, the peak area from each sample in a 120 ml bottle was equal to the sum of the peak areas from an equivalent sample of the same meal in one bottle and an equivalent sample of hexane in a separate bottle.

Other Considerations

In addition to providing more quantitative recovery of hexane, the volatilization procedure has other advantages. It is simpler than extraction or distillation. It requires only a 2 g sample, whereas the modified Todd method requires 25 g. The injection of headspace gas instead of a solution into the chromatograph eliminates the problem of column overloading, reduces the amount of interference and extends the life of the columns.

To the experimenter, however, perhaps the most attractive feature of the volatilization procedure is its negligible demand on time, essentially just weighing the sample and injecting the gas into the chromatographic column.

Other Potential Uses

Preliminary investigations indicate that the volatilization procedure is also useful for the determination of other residual solvents, such as acetone and isopropanol, and for the determination of mesityl oxide and diacetone alcohol in oilseed meals and flours processed by a solvent system containing acetone. Therefore, studies are being conducted to identify the most suitable conditions for the quantitative determination of such solvents or impurities in oilseed meals and flours and for the determination of residual solvent in oils.

TABLE II

Determination of Residual Hexane by Extraction, Distillation and Volatilization Procedures

Type of sample[a]	Hexane recovered (ppm)			
	Extraction		Distillation[b]	Volatilization
	Isooctane	DMF		
Soybean meal	ND[c]	80	60	130
Soybean meal	ND	6	8	30
Soybean flour	ND	30	.....	150
Cottonseed meal	ND	50	45	90
Cottonseed flour	ND	ND	ND	ND
Cottonseed flour	6	50	150	240
Cottonseed flour	ND	1500	1200	2700
Cottonseed flour	ND	600	750	1200

[a] The first five samples were commercial products; the other three were prepared in the laboratory or pilot plant.
[b] These values are not corrected by a factor for per cent recovery.
[c] None detectable.

ACKNOWLEDGMENTS

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