

[54] **DETERMINATION OF RESIDUAL SOLVENT IN OILSEED MEALS AND FLOURS BY A VOLATILIZATION PROCEDURE**

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[56] **References Cited**

UNITED STATES PATENTS

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Primary Examiner—Richard C. Queisser

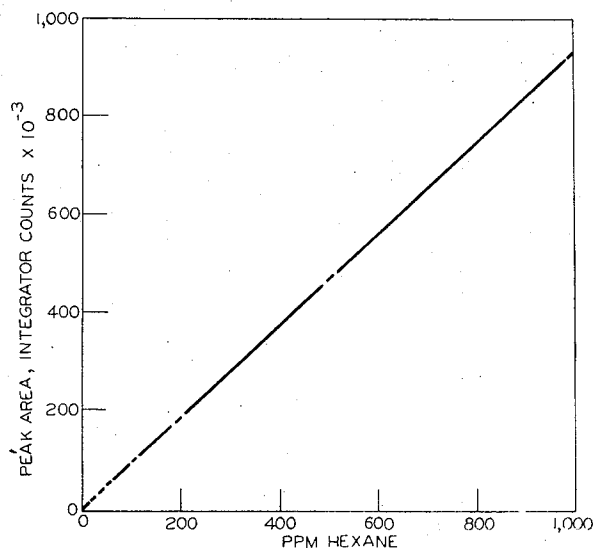
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[57] **ABSTRACT**

This invention relates to a simple volatilization procedure for the determination of residual solvents in oilseed meals and flours. A sample of meal or flour and water are weighed into a serum bottle. The bottle is sealed and heated in an oven to volatilize the residual solvent. An aliquot of the headspace gas is then analyzed by gas chromatography.

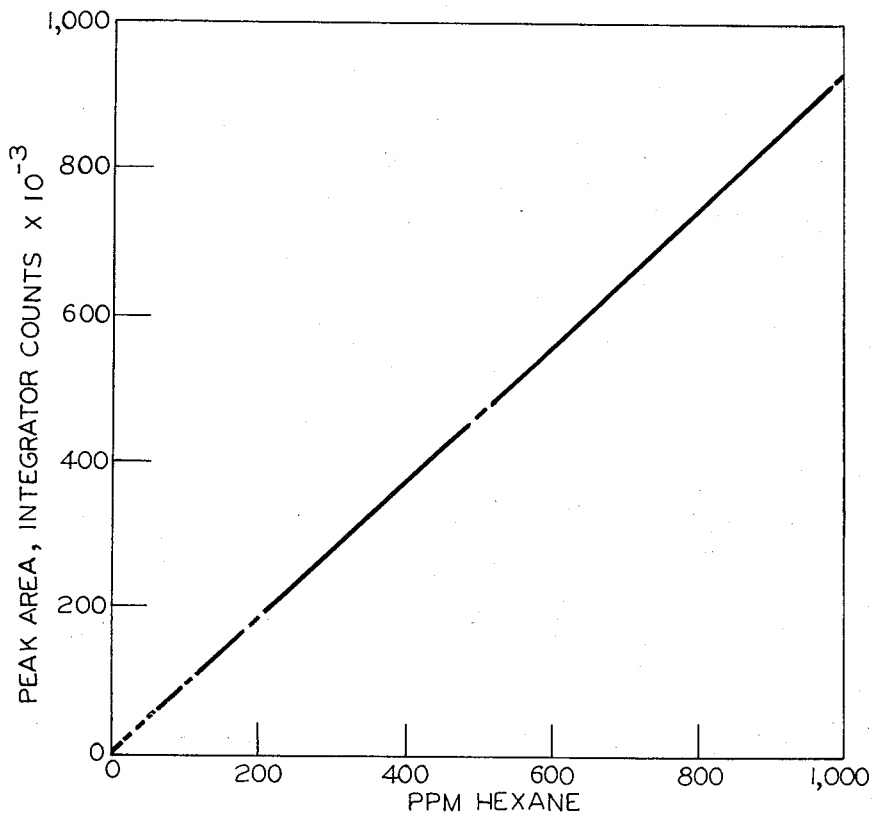
3 Claims, 1 Drawing Figure



CALIBRATION CHART FOR CONVERTING PEAK AREA COUNT TO PPM OF HEXANE

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CALIBRATION CHART FOR CONVERTING PEAK AREA
COUNT TO PPM OF HEXANE

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DETERMINATION OF RESIDUAL SOLVENT IN OILSEED MEALS AND FLOURS BY A VOLATILIZATION PROCEDURE

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of The United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of The United States of America.

In general, the procedure consists of the following: A sample of oilseed meal or flour is weighed into a serum bottle together with a small volume of water. An internal standard such as ethanol or methanol can conveniently be added to the water which is incorporated to accelerate the volatilization of the residual solvent. The serum bottle is sealed with a syringe penetrable rubber stopper and heated in an oven for a specified period to volatilize the residual solvent present in the meal or flour. An aliquot of the headspace gas is then analyzed by gas chromatography and the concentration of residual solvent in the meal or flour is easily determined by the aid of a calibration curve.

In experiments 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 necessary to determine the concentration of residual hexane and acetone which might be present in the oilseed meals. The procedure of Black and Mustakas [Black, L.T., and G. C. Mustakas, Journal of the American Oil Chemists' Society 42, 62-64 (1965)] for the determination of residual hexane in soybean flakes was investigated, but the isooctane extracting solvent did not efficiently remove the 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 percent 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.

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 solvent, such as hexane, acetone, and isopropanol in oilseed and fish meals and flours.

In order to achieve the maximum volatilization of residual solvents 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 60° and 140° C. At 60° C. it was impossible to obtain maximum volatilization of residual solvent 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 solvent with minimum decomposition of the oilseed sample could be achieved in a range of 70°-110° C. However, even at 110° C, volatilization took much too long for practical operation. In fact, some samples required as long as 25 hours.

Then an inconsistency in results suggested a solution. Residual solvents were 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 solvents 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 water markedly increased the recovery of residual solvent.

Table I, for example, shows the effect which the addition of water has on the volatilization of residual hexane from oilseed meals and flours.

TABLE I

Effect of Adding Water on the Volatilization of Residual Hexane

Hexane recovered (ppm) after 2 hr at 110° C

Type of Sample ^a	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.

In order to further establish the validity of the volatilization procedure as a means of determining residual solvents in oilseed meals and flours, the procedure was compared with three other established methods known and used for this purpose: (1) Extraction with isooctane, (2) Extraction with DMF and (3) Distillation by the Todd procedure [Todd, Paul H., Jr., Food Technology, Chicago 14, 301-305 (1960)]. Table II shows the comparative results for the determination of residual hexane in oilseed meals by all four procedures.

TABLE II

Determination of Residual Hexane by Extraction, Distillation and Volatilization Procedures

Type of sample ^a	Hexane recovered (ppm)			
	Extraction Iso-octane	DMF	Distillation ^b	Volatilization
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.

Table III shows the comparative results for the determination of residual isopropanol in oilseed meals and fish flour by the distillation and volatilization procedures.

TABLE III

Determination of Residual Isopropanol by Distillation and Volatilization Procedures

Type of Sample	Isopropanol Recovered (ppm)	
	Distillation	Volatilization
Peanut Meal	2400	2450
Peanut Meal	8	10
Fish Flour	560	620
Cottonseed Meal	2050	2200
Cottonseed Meal	1	1
Cottonseed Meal	1	1

Table IV shows the comparative results for the determination of residual acetone in oilseed meals by the distillation and volatilization procedures.

TABLE IV

Determination of Residual Acetone by Extraction, Distillation and Volatilization Procedures

Type of Sample ^a	Acetone recovered (ppm)		
	DMF Extr-action	Distillation	Volatilization
Soybean meal	ND ^b	3	4
Soybean meal	ND	6	6
Cottonseed flour	ND	8	7
Cottonseed flour	--	1	1
Cottonseed flour	80	370	400
Cottonseed flour	4	180	190
Cottonseed flour	--	50	50
Cottonseed flour	--	50	45
Cottonseed meal	--	45	45
Cottonseed meal	--	10	10
Cottonseed meal	--	12	12

^a The first three samples were commercial products; the other eight were prepared in the laboratory or pilot plant.

^b None detectable.

This simple volatilization procedure is carried out in the following manner: About 1 to 2 grams of meal or flour and about 0.2 gram of water are weighed into a 100-ml serum bottle. Although it is not necessary to use an internal standard for the determination of residual hexane, the use of ethanol as an internal standard for the determination of isopropanol and the use of methanol as an internal standard for the determination of acetone results in better reproducibility. The internal standard is easily added to the water. The serum bottle is then sealed with a syringe penetrable rubber septum and heated in an oven at about from 70° to 110° C. for a period of about from 1 to 5 hours, depending on the specific solvent to be determined. A 1 or 2 ml aliquot of the headspace gas is then analyzed by gas chromatography. The concentration of residual solvent

is then easily determined by comparing the area of the appropriate peak of the chromatogram with a calibration chart prepared by similar gas chromatographic analysis of headspace gas of known solvent concentration. Concentrations as low as 1 part per million can be detected.

The volatilization procedure is simpler, requires a much smaller sample, and is more efficient than available extraction or distillation procedures. Furthermore, the injection of headspace gas instead of a liquid solution into a gas chromatograph eliminates the problem of column over-loading, reduces the amount of interference and extends the life of the column. To the analyst, 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.

The following examples illustrate but do not limit the scope of this invention:

EXAMPLE 1

Analysis for Residual Hexane

Two grams of cottonseed meal and 0.2 g of water were weighed into a 100 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 hours, the headspace gas was ready for analysis on the gas chromatograph.

The following conditions were employed for analyzing the headspace gas. Instrument: Micro-Tek 2000 MF with dual independent hydrogen flame detectors. Recorder: Westronic LD 11 B. Integrator: Infotronics CRS-100. Columns: ¼ in. o.d. stainless steel U-tubes, (a) 1 ft Porapak P (80-100 mesh highly crosslinked polystyrene bead manufactured by the Dow Chemical Co. for use in gas chromatographic packing material), (b) 6 inch 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 headspace gas. Chart speed: 30 inch/hr.

A 1-ml aliquot of the headspace gas was removed with a plastic syringe and immediately injected into the 1 ft Porapak P column of the gas chromatograph. The digital integrator and the multilinear temperature programmer were turned on immediately. 20 seconds later, 1 ml of the headspace 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 headspace gas.

A calibration chart for use with a 2 g sample of oilseed meal or flour and a 1 ml aliquot of headspace gas was prepared as follows: Hexane (0.5 mg or 0.75 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 headspace 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 headspace 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 the accompanying drawing.

The results of representative analyses by this procedure are shown in Table II.

EXAMPLE 2

Analysis for Residual Isopropanol

One gram of meal or flour and 0.2 gram of water containing 0.075 milligram of ethanol were placed in a 100-ml serum bottle, and analysis of the headspace gas was carried out as in Example 1 with the following exceptions:

1. The sample was heated in the oven at 110° C for 1 hour.
2. An aliquot of the headspace gas was analyzed on a 1-foot Porapak Q column which was heated isothermally at 110° C.
3. A calibration curve for determining residual isopropanol was prepared.

The results of representative analyses by this procedure are shown in Table III.

EXAMPLE 3

Analysis for Residual Acetone

One gram of meal or flour and 0.2 gram of water containing 0.4 milligram of methanol were placed in a 100-ml serum bottle and the analysis of the headspace gas was carried out as in Example 1 with the following exceptions:

1. The sample was heated in the oven at 70° C for 5 hours.
2. An aliquot of the headspace gas was analyzed on a

1-foot Porapak Q column which was programmed between 70° and 180° C.

3. A calibration curve for determining residual acetone was prepared.

The results of representative analyses by this procedure are shown in Table IV.

We claim:

1. A process for determining the residual hexane content in an oilseed meal or flour, comprising:

- a. heating a mixture of about from one to two parts of an oilseed meal or flour and about from 0.01 to 0.4 part of water in a closed container at a temperature of about from 70° to 110° C. for about from one to five hours to generate headspace gas;
- b. removing an aliquot of the headspace gas from the container, and determining the hexane content thereof chromatographically.

2. A process for determining the residual isopropanol content in an oilseed meal or flour, comprising:

- a. heating a mixture of about one part of an oilseed meal or flour, about from 0.1 to 0.2 part of water, and an effective amount of ethanol as an internal standard in a closed container at a temperature of about 110° C. for about 1 hour to generate headspace gas;
- b. removing an aliquot of the headspace gas from the container, and determining the isopropanol content thereof chromatographically.

3. A process for determining the residual acetone content in an oilseed meal or flour, comprising:

- a. heating a mixture of about one part of an oilseed meal or flour, about 0.01 to 0.2 part of water, and an effective amount of methanol as an internal standard in a closed container at a temperature of about 70° C. for about five hours to generate headspace gas;
- b. removing an aliquot of the headspace gas from the container, and determining the acetone content thereof chromatographically.

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