Determination of Residual Solvent in Oilseed Meals and Flours: III. Isopropanol[1]

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ABSTRACT

A relatively simple volatilization procedure is described for the determination of residual isopropanol in oilseed meals and flours. A 1 g sample is placed in a 100 ml serum bottle, 200 μl of distilled water containing 0.075 mg of ethanol is added and the bottle is sealed with a rubber stopper and heated at 110 C for 1 hr. A 2 ml aliquot of the headspace gas is analyzed by gas chromatography using the added ethanol as an internal standard. Values determined by this procedure for three cottonseed, two peanut and two fish meals or flours which had been processed with isopropanol, ranged from 10 to 12,000 ppm and were of the same order of magnitude as values determined by a modification of the Todd azeotropic distillation procedure. Advantages of the volatilization over the azeotropic distillation procedure are that less operator and gas chromatograph time are required per analysis.

INTRODUCTION

In connection with our research program on the detoxification of mold damaged oilseed meals by isopropanol extraction, it was necessary to determine the amount of residual isopropanol remaining in the extracted meals. For this purpose, a process was developed which is essentially a modification of the volatilization procedure previously devised for determining residual hexane (1) in oilseed meals and flours. As a check on the accuracy of the volatilization procedure, the Todd azeotropic distillation procedure (2) for the determination of residual solvent in spice oleoresins was adapted to the analysis of oilseed meals. A number of samples were analyzed by both volatilization and distillation procedures.

EXPERIMENTAL PROCEDURES

Materials

All solvents were reagent grade and had been shown by gas chromatography (GC) to be of adequate purity for their intended uses. Porapak P and Q were from Waters Associates, Inc., Framingham, Mass. Serum bottles, syringe-penetratable red rubber stoppers, aluminum retainer rings and a crimper for applying the rings were from Wheaton Glass Company, Millville, N.J. Plastipak disposable syringes are manufactured by Becton, Dickinson and Co., Rutherford, N.J., and the microliter syringes were from Hamilton Co., Whittier, Calif.

Sample Preparation

Volatilization. A 1 g sample of meal and 200 μl of water containing 0.075 mg of ethanol were placed in a 100 ml serum bottle which was then sealed with a rubber stopper and aluminum retainer ring and heated in an oven at 110 C for 1 hr. A 2 ml aliquot of the headspace gas was analyzed by GC procedure A.

Azeotropic Distillation. The procedure used was that described by Todd (2) except for the following modifications: sample size was reduced from 50 to 25 g; 100 ml of 20% sodium sulfate was used instead of 10 g of sodium sulfate and 50 ml of water; 1800 ppm of benzene was used as internal standard instead of 2500 ppm; and the mixture was stirred with a magnetic stirrer during distillation.

GC Analysis

The operating conditions for GC analysis of headspace gas from the volatilization procedure (procedure A) and the toluene solution from azeotropic distillation procedure (procedure B) are the following:

Instrument. Micro-Tek 2000 MF gas chromatograph with dual independent hydrogen flame detectors, Westronics LD 11B recorder, Infotronics CRS-100 integrator.

Columns. 1/4 in. o.d., 7/21 in. i.d. stainless steel U-tubes: (A) 1 ft Porapak Q (80 - 100 mesh); (B) 2 ft Porapak P (80 - 100 mesh).

Flow Rates. Helium, 60 ml/min (each column); hydrogen, 52 ml/min (each flame); air, 1.2 cu ft/hr (fuel and scavenger gas for both flames).

TABLE I

Determination of Isopropanol by Volatilization and Azeotropic Distillation Procedures

Sample type[a]	Isopropanol, ppm	
	Volatilization	Distillation
1 Peanut meal	2300	2400
	2600	2400
2 Peanut meal	10	8
	10	---
3 Fish flour	12000	14000
	12000	---
4 Fish Flour	620	560
	620	---
5 Cottonseed meal	2300	1900
	2100	2200
6 Cottonseed meal	7000	7400
	6500	8000
7 Cottonseed meal	9000	10000
	9500	12000
8 Cottonseed meal	1	1
	1	---
9 Cottonseed meal	1	1
	1	---
10 Cottonseed meal	1	1
	1	---
11 Cottonseed flour	1	1
	1	---
12 Cottonseed meal No. 10+ 1000 ppm isopropanol	1010	980
	1020	1020
13 Cottonseed flour No. 11+ 1000 ppm isopropanol	1050	1000
	1050	900

[a]Samples 1 through 9 were laboratory preparations in which isopropanol was used; samples 10 and 11 were commercial products which had not been processed with isopropanol.

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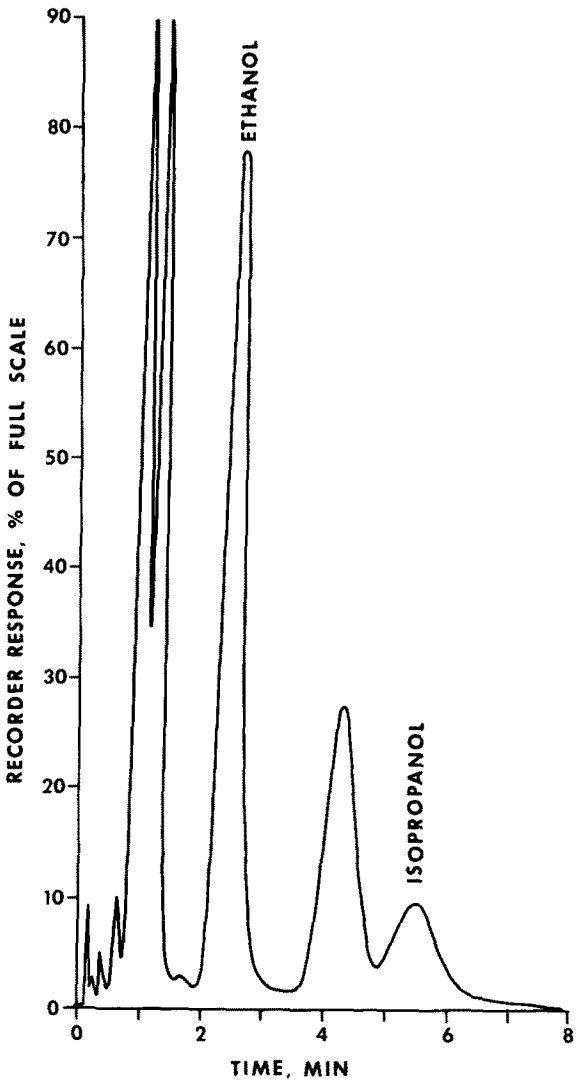

FIG. 1. GC curve obtained by the volatilization procedure of a peanut meal found to contain ca. 10 ppm of isopropanol.

Temperature. Columns: (A) isothermal at 110 C; (B) programmed 80-100 C. Initial hold, 80 C/for 2 min. Program 1, 5 C/min for 12 min. Program 2, 5 C/min for 3 min. Final hold, 180 C for 5 min. Detector: 200 C. Injector: (A) 145 C, (B) 175 C.

Sample Size. (A) 2.0 ml; (B) 0.2 μl.

Internal Standard. (A) Ethanol; (B) benzene.

Attenuation. Electrometers, 10 X 1; integrator, X 1 with automatic attenuation in steps of X 10.

Chart Speed. 30 in/hr.

Samples of headspace gas were analyzed isothermally on a Porapak Q column, while both Porapak P and Q columns and a temperature program were utilized for the analysis of samples from the azeotropic distillation procedure. Programming of the column temperature was needed to separate the large toluene peak from isopropanol and the benzene internal standard. Since some of the samples contained residual hexane, Porapak Q could not be used alone for analysis of toluene solutions as it did not separate hexane from benzene. The Porapak P column accomplished this separation but did not separate isopropanol from acetone. Most of the samples contained a compound which had the same retention time as acetone on both columns and was not resolved from isopropanol on the Porapak P column. Where the interfering peak was large enough in proportion to the isopropanol peak to be significant, the portion of the unresolved peak from the Porapak P column

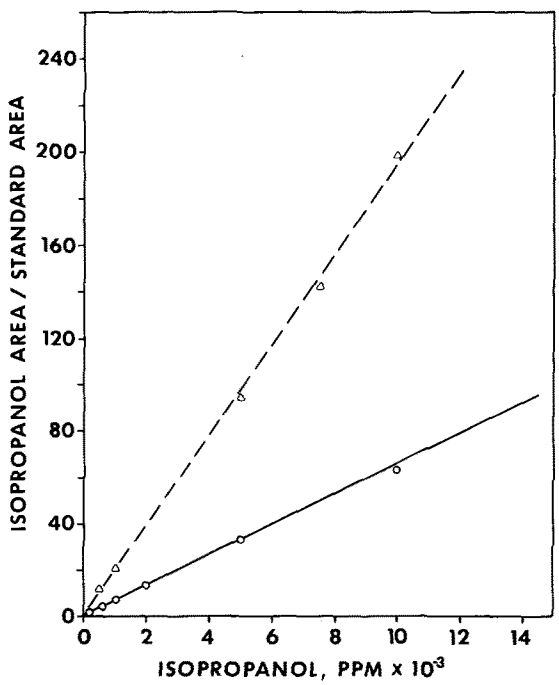

FIG. 2. Calibration curves for determination of residual isopropanol: Dotted line, volatilization procedure; solid line, azeotropic distillation procedure.

to be assigned to isopropanol was determined from the Porapak Q column.

Injections of headspace gas were made with 2.5 ml disposable syringes which were dismantled and heated at 110 C for 5 min immediately before use to prevent condensation of vapor in the syringe and to remove isopropanol from the previous run. Toluene solutions were injected with a 1 μl syringe.

A typical chromatogram from the volatilization procedure (Sample 2, Table I) is shown in Figure 1.

Standardization

Procedure A. A series of standards was prepared which contained 375 mg of ethanol and 5-50,000 mg of isopropanol per liter of water. This corresponds to 1-10,000 ppm for a 1 g sample and a 200 μl aliquot of standard. In all cases the calculated volumes of ethanol and isopropanol were added from microliter syringes of appropriate sizes to distilled water in either 1-, 2-, 5- or 10-ml volumetric flasks which were then made to volume with distilled water. A 200 μl portion of each standard was sealed into a serum bottle and heated at 110 C for 1 hr. A 2 ml aliquot of headspace gas was chromatographed by GC procedure A. The calibration curve, Figure 2, for a 1 g sample was prepared by plotting the ratio of the area of the isopropanol peak to the ethanol peak against ppm of isopropanol.

Procedure B. Using the conditions described under procedure A, a series of standards was prepared which contained 1800 mg of benzene and 25-250,000 mg of isopropanol per liter of toluene. The calibration curve for a 25 g sample of meal or flour is also shown in Figure 1.

Recovery Factors

Isopropanol, 1000 ppm, was added to cottonseed meal or flour in the serum bottle or distillation flask immediately before beginning the procedure, and analysis was carried out in the usual way. For procedure A, the isopropanol was added in the aqueous solution which contained the ethanol internal standard; and for procedure B, isopropanol was added in 1 ml of water.

RESULTS AND DISCUSSION

The three variables, temperature, time and moisture, which had been found to be important in the analysis of residual hexane were equally important in determining residual isopropanol. When enough water was present, maximum volatilization of isopropanol occurred at 110 C within 1 hr without the generation of large amounts of interfering materials. No change in the isopropanol content of the headspace gas occurred when the heating time was extended to 2 hr, so heating time is not critical within limits. As in the analysis for residual hexane, moisture was found to be the single most important factor in promoting volatilization of isopropanol. For example, a greater than tenfold increase in apparent isopropanol content was observed when 200 μl of water was added to a sample of meal which had a moisture content of 1%. The amount of added water could be varied between 150 and 400 μl without apparent effect. Therefore, when 200 μl of water is added to a 1 g sample, normal variations in the original moisture contents of the samples should not affect results.

When the residual isopropanol content of oilseed meals was less than 2500 ppm, the sample size was not a critical factor and could be varied from 1/2 to 2 g without affecting the results. However, with oilseed meals having a considerably higher residual isopropanol content, the sample size significantly affected the results, yielding progressively higher values with decreasing sample size. For example, at an isopropanol content of 20,000 ppm, results with a 1/2 g meal sample were 25% higher than results obtained with a 1 g sample. Since we were primarily interested in the quantitative determination of isopropanol in extracted meals with generally low levels of residual isopropanol, sample size did not present a problem. Good reproducibility and high sensitivity could be achieved by using a 1 g sample for all analyses.

Use of ethanol as an internal standard improved the reproducibility of the volatilization procedure. For the analyses by the volatilization procedure reported in Table II, deviation of duplicates from their averages ranged from 0% to 6%, but when the same data was recalculated without use of the internal standard, deviations ranged from 1.5% to 22%.

Since we were not certain that the volatilization procedure achieved complete recovery of residual isopropanol, the results obtained were compared with a recognized procedure. Modifications (3) of the Todd azeotropic distillation procedure (2) are used by the Food and Drug Administration for determining residual isopropanol in fish meal and spice oleoresins, therefore we adapted the Todd procedure for the analysis of isopropanol in oilseed meals. As shown in Table I, results by the two procedures are comparable.

While it is possible to detect isopropanol at the parts per million level by either technique, neither is useful at concentrations below several parts per million since there is a tendency to generate small amounts of isopropanol on heating. The values reported in Table I are uncorrected since the recovery of added isopropanol by both procedures was well within experimental error.

The volatilization procedure is simpler than the distillation procedure and requires less sample. Injection of headspace gas into the chromatograph rather than a solution, eliminates the problem of overloading the column with a large solvent peak, reduces the amount of interference and extends the life of the columns. Furthermore, the volatilization procedure requires very little operator time.

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