Determination of Residual Solvent in Oilseed Meals and Flours: IV. Acetone[1]

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ABSTRACT

A simple volatilization procedure was developed for the determination of residual acetone in oilseed meals and flours. One gram of meal or flour and 0.2 g of water containing 0.4 mg of methanol are added into a 100 ml serum bottle, which is sealed and heated at 70 C for 5 hr in an oven. A 1 ml aliquot of the headspace gas is then analyzed by gas chromatography. The concentration of residual acetone is easily determined by comparing the ratio of the peak areas of acetone to methanol of the chromatogram with a calibration curve. Results are reproducible within ± 10%, and concentrations of a few ppm can be detected. This technique is much simpler and requires less operator time than other procedures available.

INTRODUCTION

In the process of preparing oilseed meals and flours or removing mycotoxins from contaminated meals by acetone extraction, it was necessary to determine the residual content of acetone in the desolventized meals and flours. An azeotropic distillation procedure (1) and an aqueous dimethylformamide (DMF) procedure (2) were available for the determination of residual acetone; but these procedures were tedious and time consuming, and in some instances did not efficiently extract residual acetone from the processed meals and flours. Therefore, the volatilization procedure which had been developed earlier for the quantitative determination of residual hexane (3) and isopropanol (4) in oilseed meals and flours was modified to make it applicable for the determination of residual acetone in these products. A number of meals and flours were analyzed for residual acetone by this volatilization procedure and the results were compared with the results obtained with the Todd distillation procedure which was adapted to oilseed meals and flours (4).

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. Plastipak disposable plastic syringes were manufactured by Becton, Dickinson and Company, Rutherford, N.J. The syringes were placed in the oven at 70 C for about 20 min prior to use or reuse to eliminate small amounts of solvent or impurities and to prevent condensation of vapors. The commercial cottonseed or soybean meals and flours were obtained from three commercial sources.

Internal Standard

Methanol was used as an internal standard. It was conveniently added to the water (2 mg/liter) which was used to accelerate the volatilization of residual acetone from the meal or flour.

TABLE I

Determination of Residual Acetone by Extraction, Distillation and Volatilization Procedures

Type of sample[a]	Acetone recovered, ppm		
	DMF extraction	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.

Volatilization

One gram of oilseed meal or flour and 0.2 g of water containing 0.4 mg of methanol were added 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 70 C for 5 hr, a 1 ml aliquot of the headspace gas was removed with a plastic syringe and immediately injected into the 1 ft Porapak Q column of the gas chromatograph. The digital integrator and the multilinear temperature programmer were turned on immediately. Thirty seconds later, 1 ml of the headspace gas was injected into the 2 ft Porapak P column to help

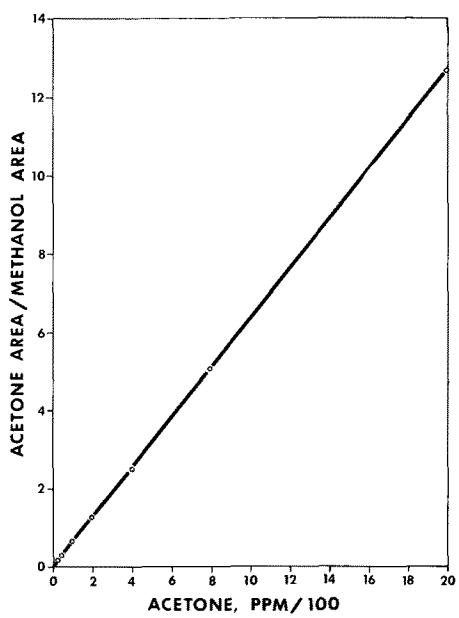

FIG. 1. Calibration curve for converting ratio of peak area counts to parts per million of acetone.

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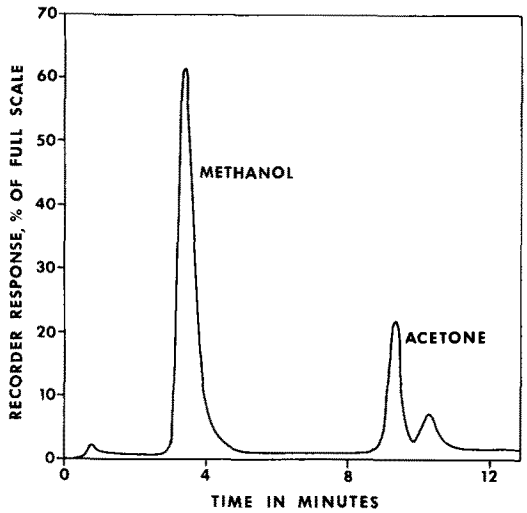

FIG. 2. Representative GC curve from a sample of cottonseed flour with a residual acetone concentration of about 50 ppm.

confirm the presence of acetone. The temperature programmer completed its cycle in 35 min, and the chromatograph was then ready for another aliquot of headspace gas. The gas chromatographic (GC) conditions employed are the following:

Instrument. MicroTek 2000 MF with 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 and 1 ft Porapak Q (80-100 mesh).

Flow rates. Helium, 60 ml/min in each column, Hydrogen, 52 ml/min to each flame, Air, 1.2 ft^3/hr (fuel and scavenger gas).

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 5 min, Programmed at 5 C/min for 5 min, Programmed at 10 C/min for 3 min, Final hold at 180 C for 8 min.

Attenuation. 10 X 1 for both electrometers, Auto X 1 for integrator.

Sample size. 1 ml of headspace gas.

Chart speed. 30 in./hr.

Standardization

A calibration curve for use with a 1 g sample of oilseed meal or flour and a 1 ml aliquot of headspace gas was prepared. One gram of cottonseed flour which was prepared from screw-pressed cake and 0.2 g of water containing 0.4 mg of methanol were added to each of seven 100 ml serum bottles which were immediately sealed with red rubber septums. A series of standards was prepared by injecting 0.02 mg, 0.04 mg, 0.1 mg, 0.2 mg, 0.4 mg, 0.8 mg and 2.0 mg of acetone in these bottles. After each bottle had been heated at 70 C in an oven for 5 hr, a 1 ml aliquot of the headspace gas was injected into the Porapak Q column of the gas chromatograph. The calibration curve was constructed by plotting the ratio of the peak areas of acetone to methanol against the concentration of acetone in parts per million of flour. The calibration curve is shown in Figure 1.

RESULTS AND DISCUSSION

In preliminary studies of the volatilization procedure, samples of meals and flours were heated to 110 C, and it was not possible to obtain a maximum concentration of acetone in the headspace gas. Numerous analyses revealed that acetone was being generated in the oilseed meals and flours by heating at this temperature, and the concentration of acetone in the headspace gas gradually increased with time. This observation was confirmed by mass spectroscopic analysis of the headspace gas from heated meals and flours which had not been processed with acetone.

Thus in order to achieve maximum volatilization of residual acetone and also minimize the generation of acetone from samples of oilseed meals and flours, it was necessary to maintain a careful balance of the interaction of the three variables, temperature, time and moisture. The results from numerous experiments indicated that the generation of acetone was greatly reduced or eliminated by lowering the volatilization temperature to 70 C. Also volatilization of residual acetone in the meals and flours was greatly enhanced by the addition of water.

Based on numerous analyses, effective volatilization of residual acetone in meals and flours was achieved by heating a one g sample at 70 C for about 5 hr in the presence of 20% additional water, and the results were reproducible within ± 10%. A representative curve obtained by gas chromatography is shown in Figure 2.

The fact that the volatilization process yields complete recovery of acetone added to meals and flours (as in the preparation of the calibration curve) does not ensure complete recovery of residual acetone. Residual acetone in solvent extracted meals and flours is more difficult to volatilize since it appears to be strongly bound or trapped. Therefore, recovery of residual acetone by the volatilization procedure was compared with recovery of residual acetone by the Todd distillation procedure (1).

For this purpose, the Todd procedure was adapted to oilseed meals and flours (4). Since complete recovery of added acetone was obtained, it was not necessary to apply a recovery factor.

The results obtained for residual acetone on oilseed meals and flours by the volatilization and distillation procedures compare very well as shown in Table I. It is possible to detect acetone at the parts per million level by both techniques, but neither one is useful for the determination of residual acetone at concentrations below several ppm since there is a slight tendency to generate small amounts of acetone from oilseed meals and flours by heating.

While the two procedures are equally effective, the volatilization procedure is much simpler and requires less sample and little operator time. The use of headspace gas instead of liquid in gas chromatography eliminates the problem of column overloading and minimizes the amount of interference. Because of the reduced interference, the volatilization procedure also permits detection of acetone condensation products such as mesityl oxide and diacetone alcohol, if these are present in the sample. These compounds normally cannot be resolved from the large peak produced by the toluene solvent used in the distillation procedure.

REFERENCES

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