Determination of Residual Solvent in Oilseed Meals and Flours: I. Dimethyl Formamide Extraction Procedure

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Abstract

A procedure is described for determination of residual acetone and hexane in cottonseed and soybean meals and flours by extraction of the residual solvent with dimethyl formamide (DMF)-water (95:5) followed by gas liquid chromatography analysis of the DMF extracts. A representative group of samples was analyzed both by this procedure and one employing isooctane as extractant. In all cases where residual solvent was found, the amount was markedly greater when aqueous DMF was the extracting solvent.

Introduction

In connection with work on the off-flavors observed in acetone-hexane-water (AHW) extracted cottonseed flours (1), it was desirable to determine the amounts of residual acetone and hexane present in these flours. The possibility of using a modification of the procedure proposed by Black and Mustakas (2) for the determination of residual hexane in soybean flakes was investigated. Their procedure involves the extraction of residual hexane with isooctane followed by GLC determination of the hexane content of the isooctane extract. However, since our initial experiments indicated that isooctane did not efficiently remove residual solvent from AHW processed cottonseed flours, a number of ethers, ketones and formamides were screened as extractants. The most promising of these was dimethyl formamide (DMF) to which 5% of water had been added. Accordingly, procedures for extraction and gas liquid chromatographic (GLC) analysis of extracts were developed using both aqueous DMF and isooctane as extracting solvents. In order to determine whether the apparent superiority of aqueous DMF to isooctane as an extractant for residual hexane and acetone was confined to AHW cottonseed flours or was of more general applicability, 13 cottonseed and soybean meals and flours from a variety of sources were analyzed by both procedures.

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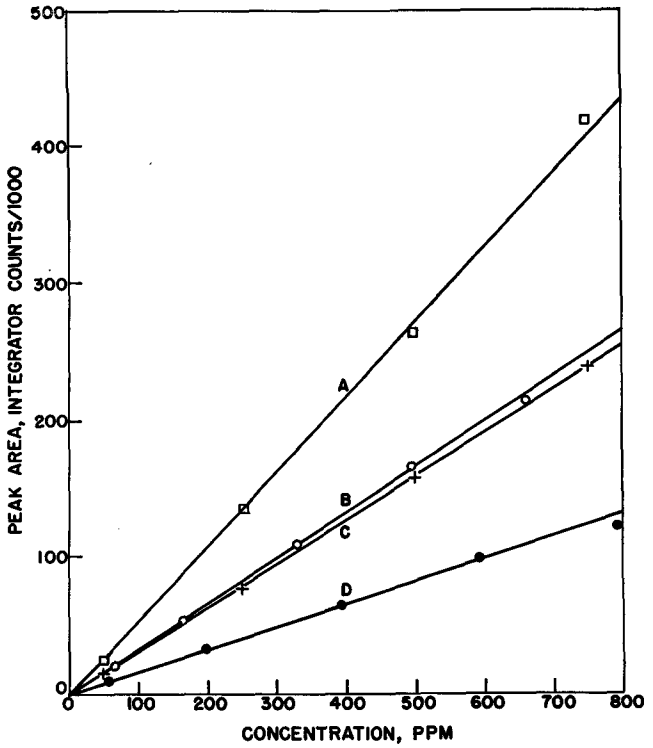

FIG. 1. Calibration curves: A, hexane in isooctane, procedure a; B, hexane in DMF, procedure b; C, acetone in isooctane, procedure a; D, acetone in DMF, procedure b.

Procedures and Results

Materials

Eastman spectrograde DMF (N,N-dimethylformamide) and isooctane (2,2,4-trimethylpentane), Mallinckrodt analytical reagent grade acetone and technical grade hexane (Skellysolve B) were all found by GLC analysis to be sufficiently pure to use without purification. Porapak P and Q, both 80–100 mesh, were obtained from Waters Associates, Inc., Framingham, Mass. The commercial cottonseed and soybean meals and flours used in this work were from four different commercial sources.

Extraction Procedure

The extractions were carried out in 10 ml bottles

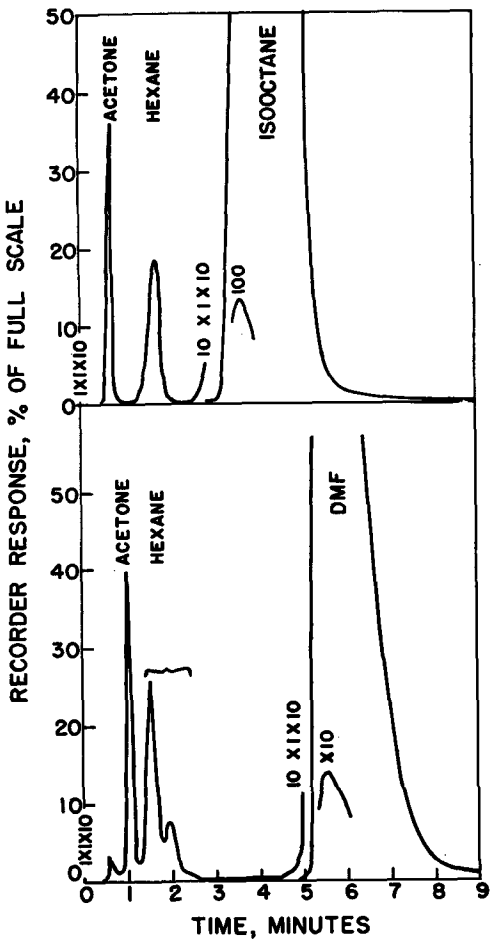

FIG. 2. Representative GLC curves: Top curve acetone, 79 ppm, and hexane, 66 ppm, in isooctane, procedure a. Bottom curve acetone, 158 ppm, and hexane, 132 ppm, in DMF, procedure b.

TABLE I

Residual Acetone and Hexane in Cottonseed and Soybean Flours and Meals[a]

Sample	Description[b]	Solvent used in preparation		Acetone, ppm		Hexane, ppm	
				Extracting solvent		Extracting solvent	
		Acetone	Hexane	DMF–H_2O	Isooctane	DMF–H_2O	Isooctane
1	Soybean meal		X	ND[c]	ND	80	ND
2	Soybean meal		X	ND	ND	6	ND
3	Soybean flour		X	ND	ND	30	ND
4	Cottonseed meal		X	ND	ND	50	ND
5	Cottonseed flour		X	ND	ND	50	6
6	Cottonseed flour	X	X	80	20	1500	ND
7	Cottonseed flour	X	X	4	ND	ND	ND
8	Cottonseed flour	X	X	ND	ND	600	ND
9	Cottonseed flour[d]	X	X	ND	ND	30	ND
10	Cottonseed flour	X		80	6	ND	ND

[a] No acetone or hexane was found by either procedure in a commercial, pressed, cottonseed flour; one commercial, hexane-extracted, cottonseed meal; or one pilot plant, hexane-extracted, cottonseed flour.
[b] Samples 1–4 and 7 are commercial products, 6 was extracted in our pilot plant and commercially desolventized, 5 was obtained by grinding commercially prepared cottonseed flakes, and 8–10 were our laboratory or pilot-plant preparations.
[c] ND means none detected. The lower limit of detection is about 4 ppm in the meal or flour if complete extraction of residual solvent is assumed.
[d] Solvent-free cottonseed flour was wet with acetone and hexane and air dried for 72 hr and then allowed to equilibrate in a closed container for at least 24 hr.

fitted with red rubber stoppers and aluminum retainer rings (Wheaton Glass Co., Millville, N.J). In order to minimize loss of residual solvent from the sample, the bottle and cap were first weighed, the sample (1.5–2.5 g) was added rapidly and the bottle was stoppered and weighed after which the stopper was removed only long enough to pipette in 2 ml of extracting solvent, either DMF-water (95:5) or isooctane per gram of sample. The stopper was then secured with the aluminum retainer ring and the sample was shaken on a rocking type shaker for 1 hr if finely ground or 2 hr if coarsely ground. The samples were then centrifuged for 10 min after which aliquots of the supernatant liquid were withdrawn by syringe for GLC analysis. Increasing the shaking time by 1 hr did not affect the results.

Gas Chromatographic Conditions

The conditions employed for the quantitative determination of acetone and hexane in solution in isooctane and DMF-water, GLC procedures a and b respectively, are the following:

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′ Poropak Q (80–100 mesh); (b) 2′ Poropak P (80–100 mesh).

Carrier gas. Helium.

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).

Temperature. Column, (a) 175 C, (b) 125 C; detector, 200 C; injector, 190 C.

Attenuation. Electrometer, 1 × 1 for residual solvent peaks, 10^2 × 1 for extractant; integrator output, × 10 with automatic attenuation in steps of × 10.

Sample size. (a) 0.9 μl; (b) 0.5 μl.

Chart speed. 30 sec/hr.

In practice, since about 25 min was required after sample injection for the baseline to return to normal, two columns of each type were prepared and these were used alternately.

Standardization

All four of the columns used in this work were standardized using at least six different concentrations of acetone and hexane in the appropriate solvent. Solutions were prepared by adding a calculated amount of acetone and hexane from a microliter syringe of appropriate size to 10 or 100 ml portions, measured by pipette, of aqueous DMF or isooctane contained in serum bottles sealed with syringe penetratable red rubber stoppers. Samples for GLC analysis were withdrawn by syringe through the stopper. Each point on the calibration plots is the average of two determinations. Calibration curves and typical GLC curves are given for one column only for each procedure in Figures 1 and 2. The minimum amount of either hexane or acetone which could be reliably detected in a standard solution by either procedure was about 2 ppm. Consequently, if extraction of the residual solvent from the flour is complete, the minimum amount of residual solvent detectable by either procedure is 4 ppm.

Thirteen samples of cottonseed and soybean meals and flours were analyzed by both the aqueous DMF and isooctane extraction procedures. Duplicate extractions were made with each solvent and each of the extracts was analyzed in duplicate by the appropriate GLC procedure. The averages of the results obtained with each solvent for the samples are given in Table I. In order to confirm the identity of the acetone and hexane peaks obtained from the aqueous DMF extracts of the samples, these extracts were also chromatographed by GLC procedure a. This procedure could not be used for quantitative analysis of aqueous DMF solutions; however, as peaks which were generated by water in the DMF and increased in intensity by water extracted from the samples by DMF, added to the intensity of the acetone and hexane peaks.

Discussion

Although it is not possible to say whether or not aqueous DMF extracts all residual solvent from oilseed meals and flours, it is evident from the data in Table II that it is far superior to isooctane for this purpose. That the compounds extracted from the samples by aqueous DMF are actually acetone and hexane is confirmed by the fact that both peak shapes and retention times conform to those of the known compounds on two different chromatographic columns. The fact that added hexane could be extracted from a previously solvent-free cottonseed flour with aqueous DMF but not with isooctane is further evidence that residual hexane is more readily extracted with the former. Because of the uncertainty as to whether or not all residual acetone and hexane are extracted even with aqueous DMF, investigation of the determination of residual solvents in oilseed flours is being continued.

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