Composition of Residual Solvent in Oilseed Marc Extracted With Aqueous Mixed Solvents[1]

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ABSTRACT

The amount and composition of residual solvent adhering to, or absorbed by extracted oilseed meats is important in research on the design and control of mixed solvent extraction processes. A rapid method requiring unsophisticated apparatus and instrumentation usually available in oilseed processing laboratories for analysis of the extracted marc is described. This method consists of azeotropic distillation of the solvent from the marc followed by centrifugation of the double-phase distillate in calibrated oil centrifuge tubes, reading the volumes of the lower layers, and obtaining the water content from this reading, and a graph, previously constructed by applying the method to known mixtures. Total volatile matter is determined by evaporation and oven drying. Equations for calculating other volatile components of the marc are given. Data are shown for the recovery and quantitative determination of water, and equations are given for calculating acetone and hexane contents in cottonseed marc extracted with a mixture of these solvents.

INTRODUCTION

Modern research on oilseed processing methods to remove the oil and to condition the proteinaceous residue for subsequent specialized uses has shown that unique protein products may result from extraction of the seed with aqueous mixed solvents (1,2). Nonpolar components of the extraction solvent mixture, such as volatile hydrocarbons, are used to efficiently extract the oil. Polar solvents, such as the relatively chemically inert volatile alcohols and ketones, as well as water, have been found to be desirable components of the extraction solvent mixture (3,4).

The procedure described herein was considered convenient from the standpoint of equipment and sample preparation, requiring minimum time and equipment for analysis of residual solvent in the complex mixtures likely to be encountered. It was believed that a simple method, taking advantage of the phase separation in the toluene distillate, would be less time-consuming as well as more precise and accurate. Furthermore, the unsophisticated equipment requirements involving only the usual laboratory distillation apparatus and a centrifuge may be an advantage.

Preliminary experiments indicated that relatively nonpolar solvents such as the saturated aliphatic hydrocarbons (e.g., hexane and heptane) and aromatic hydrocarbons (benzene and its homologs) formed two liquid phases when mixed with volatile alcohols. The distribution varies with the hydrocarbon loading of the alcohol molecule. While procedures were developed for analysis of a number of combinations of polar and nonpolar solvents in oilseed marc, only one will be discussed here since the same principles apply to all such mixtures in general, needing only judicious experimental application of the principles.

MATERIALS AND METHODS

The solvent combination chosen for this example consisted of a mixture of acetone, hexane and water in a volume ratio of 53:44:3. This corresponds to a weight ratio of 57:39:4. This combination has been successfully used to extract the oil and pigments from decorticated, flaked, raw cottonseed meats. Several portions of the solvent mixture were used in countercurrent extraction and it was found that the flakes preferentially absorbed water from the mixed solvent, thus changing the composition of the solvent as well as that of the marc. It was necessary to know the changing water content of the marc and the solvent to intelligently interpret the results of the extraction and to devise means of recovering the solvent for reuse, and for drying the marc.

The ternary mixture of acetone-hexane-water used distills at 50 C [under conditions prevailing in a "rising film" evaporator such as those used for solvent recovery in vegetable oil mills. The true azeotrope, having a composition of 56.5% hexane, 42.1% acetone and 1.4% water is obtained only by efficient rectification of the ternary mixture in a rectifying column. This azeotrope boils at 49 C. (3)]. When flaked, raw, decorticated cottonseed meats are extracted with this solvent some of the water is absorbed by the meats. The miscella contains acetone and hexane in the proportion of 59% of acetone to 41% hexane and various amounts of the original moisture of the seed, oil and nonvolatile extractives, including sugars and phosphatides. Part of this miscella adheres to the moist flakes after extraction. It was found that when the solvent-damp, moist marc with its adhering miscella is subjected to toluene distillation all of the volatile material distills with the toluene. This includes all of the absorbed water, together with the original moisture of the raw, flaked meats. It was also found that when raw, flaked cottonseed meats are subjected to toluene distillation quantitative recovery of the natural moisture present results and no water is generated by decomposition of the protein component at the temperature of boiling toluene since the loss in weight obtained on drying is equivalent to the water obtained by distillation.

A marc consisting of spent cottonseed flakes which had been extracted with the acetone-hexane-water mixture was used for the experiments. Approximately 5 g of the mixture were weighed into a covered dish. The organic

TABLE I

Recovery Data

Grams H_2O in sample	% Recovery
0.5	100
0.8	106
1.0	100
1.6	100
1.6	107
2.0	100
2.3	104
2.5	104
3.0	93
3.0	100
3.5	97
Average	100

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solvent was removed on a steam bath and the residue was dried by the AOCS method for moisture in cottonseed meal (5). The total loss in weight was calculated as total volatile matter (TVM). For the water determination, the sample weight for the toluene distillation step was calculated from Equation 1.

$$\text{Sample weight} = 2000/\%\,\text{TVM} \qquad [1]$$

This calculation adjusts the sample weight to give a sufficiently constant amount of acetone and hexane to adjust the partition of the distillate so the calibration graph can be duplicated. The amount of water usually falls within the range of the measuring equipment. The variable component is water which has two sources: the solvent, and the natural moisture of the meats. The ratio of hexane to acetone remains constant and the amount of the mixture present in the marc can be calculated from Equation 2.

$$\%\,\text{Acetone-hexane} = \%\,\text{VTM} - \%\,\text{water} \qquad [2]$$

Since the acetone-hexane ratio remains constant the relationships of Equations 3 and 4 hold.

$$\%\,\text{Acetone} = 0.59\,(\%\,\text{TVM} - \%\,\text{water}) \qquad [3]$$

$$\%\,\text{Hexane} = 0.41\,(\%\,\text{TVM} - \%\,\text{water}) \qquad [4]$$

Consequently the weight percentages of hexane and acetone can be calculated from the determined TVM and water contents.

Brief details for determination of water content follow. The calculated amount of sample was weighed by difference into a 1 liter pyrex flask equipped with a standard-taper connection. Four hundred milliliters of toluene were added and the flask was connected to a distilling apparatus consisting of an 18 in. West condenser with an adapter connected to the exit. Standard-taper fittings were used throughout. The bottom portion of an electric heating mantle was connected with a variable transformer and used for the distillation. With the water flowing through the condenser jacket, 50 ml of distillate were collected in a 100 ml oil centrifuge tube calibrated to 3.0 ml in the lower stem and at the 50 and 100 ml marks. When the 50 ml mark was reached, the cooling water was drained from the condenser jacket. The distillation was continued without interruption until the 100 ml mark was reached. This was necessary to force droplets of water through the condenser into the measuring tube. At that point another oil tube was substituted and the cooling water was turned on again and the distillation continued as before until 100 ml of distillate were obtained. This serves as a visible check on completeness of recovery of the water and provides a balance tube for the centrifuge at the same time. After cooling, the stoppered tubes and contents were mixed by hand shaking and the centrifuged at 1000 rpm for 5 min. (Centrifuging is necessary for complete separation of the aqueous and toluene phases.) The volumes of the lower layers in each tube were·read. From a previously constructed graph, developed by the method from known mixtures, the amount of water corresponding to the first tube reading was determined and the weight per cent of water in the sample was calculated from Equation 5.

$$\text{Water}\,(\%) = \frac{(\text{ml water in tube 1 plus ml lower layer in tube 2})\ 100}{\text{Weight of original sample of marc}} \qquad [5]$$

Range of the Method

If the lower layer in tube 1 exceeds the 3.0 ml maximum calibration mark repeat the determination using one half of the original sample weight and add 12 ml of a 55 to 45 mixture (by volume) of acetone and hexane. Calculate the water content using the same equation.

RESULTS AND DISCUSSION

Recovery Data

Recovery data obtained by analysis of known mixtures by the method are shown in Table I. These results show that individual determinations can be expected to give correct results within ±10%. The method has been found to be sufficiently reliable for use in pilot-plant studies of extraction processes.

REFERENCES

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