of the meniscus of the water phase), which on standing increased to give a maximum positive value. This is an important phenomenon. According to King and Mukherjee (16), emulsion stability is related to change in the area of the interface with time.

Crude rice oil was found to be effective in lowering the interfacial tension of a refined oil, when admixed with the latter. For example, refined and bleached olive oil had an interfacial tension of 17.6 dynes cm^{-1} at 25°. On adding 2% of crude rice oil, the interfacial tension was lowered to 8.1 dynes cm^{-1}, and 11% of crude rice oil lowered the value to 6.3 dynes cm^{-1}.

The difference in interfacial tensions of a crude oil and the corresponding refined oil apparently is due to some material which is removed by the normal refining procedure. That this material is not completely in the unsaponifiable matter was determined by concentrating the unsaponifiable matter of olive oil and adding this material back to refined cottonseed and olive oils, as indicated in Table III.

TABLE III

Surface and Interfacial Tensions at 25° of Refined Oils Containing Added Unsaponifiable Matter

Unsaponifiables, weight percentage	Refined cottonseed oil		Refined olive oil	
	Surface tension, dyne cm^{-1}	Interfacial tension, dyne cm^{-1}	Surface tension, dyne cm^{-1}	Interfacial tension, dyne cm^{-1}
0	30.8	14.9	28.6	17.6
2	31.2	17.9	29.5	20.5
4	30.0	15.5	27.6	18.0
10	25.3	11.9	25.3	12.9

It can be seen that there was an initial rise in the surface and interfacial tension values of both oils, followed by a decrease as the content of unsaponifiable matter was increased. It might be mentioned that 10% by weight of unsaponifiable matter represents at least a ten-fold increase over the amount naturally present in vegetable oils.

On the basis of surface phenomena alone, the crude oils investigated should be more easily emulsified than the refined oils if no added emulsifiers are used. What the effects of the non-glycerides in the crude oils would be, physiologically, is another matter. However the addition of very small amounts of emulsifying agents to the refined oils, as indicated, is sufficient to lower their interfacial tensions to the easily emulsifiable range.

Summary

Surface tensions of natural vegetable oils of known origin and processing conditions have been measured over the temperature range 25°-27° by means of a modification of the capillary rise method. Interfacial tensions against water of the crude and refined oils have been determined at 25°. The surface tensions and interfacial tensions against water of 1,3-dipalmito-2-lactin at 75° and of a synthetic fat at 55° have been determined.

The method of Least Squares was applied to the surface tension-temperature data to obtain equations of the form, $\gamma = a - bt$, where γ is the surface tension in dynes cm^{-1}, t is the temperature in °C., and a and b are the least square factors.

Only the crude rice, olive, and cottonseed oils have interfacial tensions against water less than 10 dynes cm^{-1}. Of the refined oils, coconut oil has the lowest interfacial tension, namely 12.8 dynes cm^{-1}. All of the other refined oils have interfacial tensions between 14.5 and 22.9 dynes cm^{-1} at 25°. The addition of unsaponifiable matter to a refined oil had little effect on its interfacial tension, but the addition of a small percentage of a crude oil to a refined oil lowered the interfacial tension of the refined oil considerably.

Acknowledgment

The authors are indebted to the Engineering and Development Section of the Southern Regional Research Laboratory for assistance in producing the cold-pressed peanut oil.

REFERENCES

1. Singleton, W. S., and Benerito, Ruth R., Federation Proc. *13*, 298 (1954).
2. Harkins, W. D., and Zollman, J. Am. Chem. Soc., *48*, 69 (1926).
3. Quincke, G., Pogg. Ann., *139*, 1 (1870).
4. Pound, J. R., J. Chem. Soc., *123*, 578 (1923).
5. Pound, J. R., J. Phys. Chem., *30*, 791 (1926).
6. Pound, J. R., J. Phys. Chem., *40*, 973 (1936).
7. Halpern, A., J. Phys. and Coll. Chem., *53*, 895 (1949).
8. Bailey, A. E., "Industrial Oil and Fat Products," New York, p. 540 (1951).
9. Goldblatt, L. A., Abstract of Paper No. 23, Division of Organic Chemistry, American Chemical Society, 125th Meeting, Kansas City, March (1954).
10. American Oil Chemists' Society, "Official and Tentative Methods," 2nd ed., edited by V. C. Mehlenbacher, Chicago (1946).
11. Bailey, A. E., and Feuge, R. O., Ind. Eng. Chem., Anal. Ed., *15*, 280 (1943).
12. Ferguson, A., Proc. Phys. Soc., *36*, 37 (1923).
13. Ferguson, A., and Kennedy, S. J., *Proc. Phys. Soc., 44*, 511 (1932).
14. Nevin, C. S., Althouse, P. M., and Triebold, H. O., J. Am. Oil Chemists' Soc., *28*, 325 (1951).
15. Harkins, W. D., and Brown, F. E., J. Am. Chem. Soc., *41*, 449 (1919).
16. King, A., and Mukherjee, L. N., J. Soc. Chem. Ind., *58*, 243 (1939).

[Received June 17, 1954]

Solvent Extraction of Meat Offal

L. K. ARNOLD, professor of Chemical Engineering, and H. C. ARVIDSON JR.,[1] formerly graduate assistant, Iowa Engineering Experiment Station, Iowa State College, Ames, Iowa

THE application of solvent extraction to the removal of oil from vegetable oil seeds has been extensively investigated by many, but this application has not been reported for meat offal. Similarly, the use of the Iowa State College extractor for the extraction of soybeans, cottonseed, and other vegetable oil seeds has been reported by Arnold and coworkers (4, 6). It was considered a natural extension of the work with this extractor to determine the effects of the various operating variables on the extraction of an animal material as meat offal both in the laboratory and in the pilot plant.

The material used in these studies was meat and bone scrap[2] which is produced from the wastes of the meat packing industry. This material, after having been passed through a hogger, had been dry-cooked to coagulate the protein of the meat and to reduce moisture content. The meat and bone scrap contained

[1] Present address: E. I. du Pont de Nemours, Wilmington, Del.

[2] Supplied through the courtesy of Rath Packing Co., Waterloo, Ia.

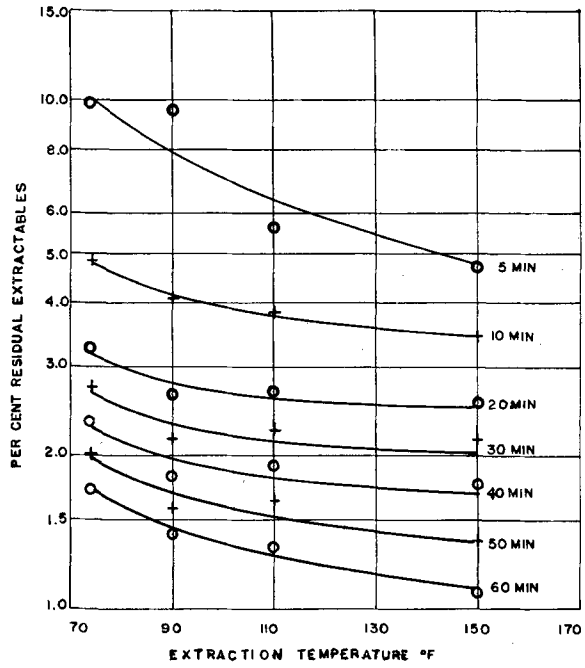

FIG. 1. Variation of residual extractables with temperature. Moisture content, 2.8%; residual extractables calculated on moisture-free basis. For screen analysis of scrap see Table I.

about 37 to 45% bones, 35 to 40% fat, and 5 to 10% moisture. The bone content was determined by hand-sorting and weighing. Fat was determined by extracting 4 hours in a Soxhlet extractor. Moisture was determined by drying at 75°C. for 4 hours. It was necessary to remove many of the bones in order to reduce the possibility of damage to the size-reduction equipment and the extractor.

For the small scale laboratory phase of this study the meat and bone scrap was passed through a Universal No. 2 food chopper with a coarse cutter plate. For the pilot plant study the material was processed through a John Deere No. 10-A hammer mill at 2,180 r.p.m. and with no screen. These preparation methods produced meat and bone scrap with the screen analyses given in Table I.

TABLE I

Screen Analysis of Meat and Bone Scrap

U. S. Screen Size	Screen opening, inches	Percentage passing screen	
		Laboratory	Pilot plant
—	0.371	95.1	90.5
3	0.263	75.0	82.7
4	0.185	47.9	68.1
6	0.131	30.2	56.8
8	0.093	17.3	36.3
12	0.065	7.1	8.7

Laboratory Phase

Laboratory rate extractions were carried out in a jacketed 1-in. glass tube with the necessary accessories to maintain constant temperature in the static bed of material and in the incoming solvent (2). The solvent used was trichloroethylene, and it was passed through 20 g. of meat and bone scrap at a rate to give an overflow of miscella of 10 milliliters per minute.

These extraction rate experiments were carried out with temperature, moisture, and particle size as the variables. The results of these tests are shown in Figures 1, 2, and 3. It will be noted that the effect of temperature was very slight after extraction periods of 5 minutes. This was due to the slight effect of temperature on the viscosity and density of the extracting solution since in rate extractions the solution is almost pure solvent.

The effect of moisture upon extraction appears to be at a minimum at about 7% moisture. Above this minimum the extraction was retarded because of poor wetting of the meat and bone scrap particles by the organic solvent trichloroethylene. Below a moisture of 7% the extraction was retarded in the diffusional portion of the rate extraction because the capillaries from which the oil was removed had been constricted. This constriction is believed to have occurred during the drying operation as a result of particle shrinkage.

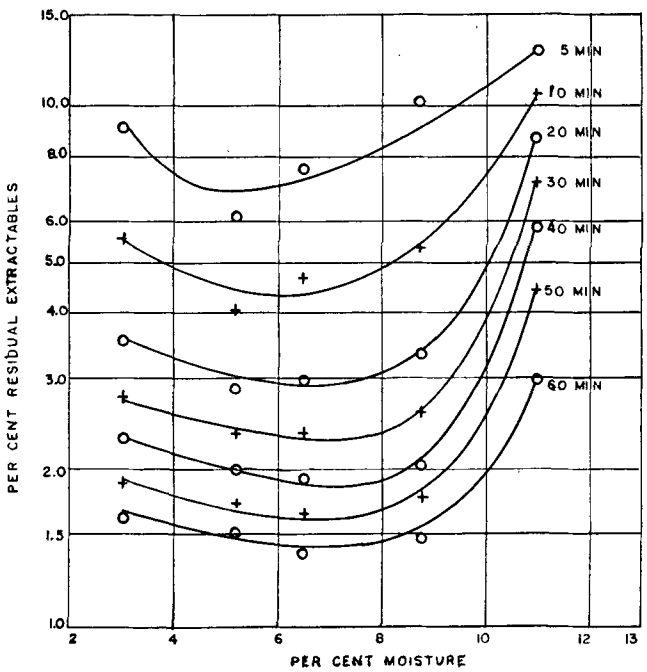

FIG. 2. Variation of residual extractables with moisture. Residual extractables calculated to moisture-free basis. Extraction temperature, 110°F. Screen analysis in Table I.

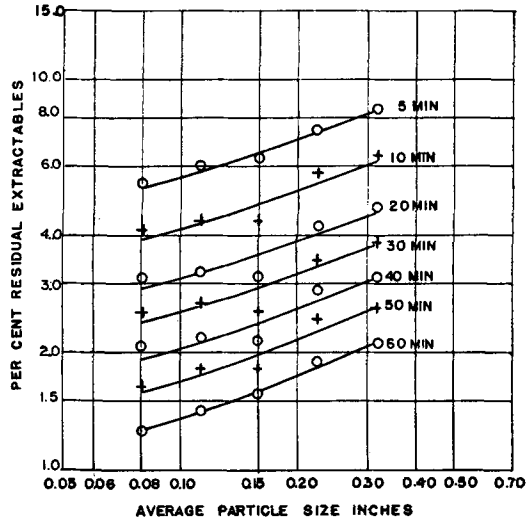

FIG. 3. Variation of residual extractables with particle size. Average particle size was calculated as the arithmetical average of the retained screen opening and the next largest screen opening. Extraction temperature 110°F. Moisture contents corresponding to various particle sizes are as follows: 0.08, 10.1%; 0.11, 10.0%; 0.16,9.2%; 0.22, 10.3%; and 0.32, 12.0%.

The shape of the curves are similar to those reported by Arnold and Patel (2) for soybeans and cottonseed.

The variation in residual extractables[3] with particle size was very consistent regardless of the time of the extraction increment selected. The data cannot be extrapolated to larger or smaller particles because, outside of the range shown, the trend does not continue. For larger particles the extraction is improved because the particles are no longer discrete but are agglomerates of smaller particles. Particles smaller than 12 mesh tend to pack together and solvent flow is retarded as is evidenced by poorer extraction. It was found experimentally with small particles that the solvent flow had to be adjusted frequently in order to maintain a constant overflow miscella rate.

Pilot Plant Phase

The extractor used in the pilot plant studies was a small model of the Iowa State College extractor originally developed by Sweeney and Arnold (6) and was used in the work reported by Arnold and P'Pool (3) and Arnold and Juhl (1). The capacity of this extractor varied from 4.24 lbs. per hour at an extraction time of 52 minutes to 12.72 lbs. per hour at an extraction time of 18.1 minutes. It was found necessary in these investigations to modify the extractor by installing a device to remove the bones at the lowest point in the extractor in order to prevent undue damage to the conveyor flights. This device consisted of a settling chamber and a screw conveyor which removed the bones continuously from the extractor. It is not believed that a deboning device would be necessary in a commercial installation.

The effects of miscella concentration, extraction time, and temperature were studied with trichloroethylene as the solvent. These results are given in Figures 4, 5, and 6 (dotted line). Following the collection of data on the extraction with trichloroethylene, an extraction run was made at the best industrial conditions with commercial hexane (Skellysolve B). The data from the run with hexane are given in Table II.

TABLE II

Extraction of Meat and Bone Scrap with Commercial Hexane

Extraction temperature	130°F.
Extraction time	26.0 min.
Miscella concentration	14.56%
Moisture content of feed	5.46%
Residual extractables hexane soxhlet	1.80%
Residual extractables trichloroethylene soxhlet	2.09%
Residual extractables (trichloroethylene extraction) trichloroethylene soxhlet	1.56%

Assuming that the data for miscella concentrations below 22% can be approximated by a straight line (Figure 4), the original data for Figures 5 and 6 were adjusted to an arbitrary miscella concentration of 20%. This concentration of 20% is frequently used in solvent-extraction of oils, such as soybean oil, and it is a readily obtainable concentration in the extraction of meat and bone scrap. The adjustment of the data was made by multiplying the actual residual extractables by the ratio of the residual extractables at 20% miscella to the residual extractables at the miscella concentration under consideration. Both values of the residual extractables for the ratio were obtained from Figure 4. The validity of this correction method has been shown by Juhl (1) for cottonseed extraction and for the present data by the fact that the form of the corrected and uncorrected data for the effect of extraction time is the same (Figure 5).

[3]Residual extractables are determined by means of a Soxhlet extraction with trichloroethylene as the solvent. The ratio of hexane extractables to trichloroethylene extractables was found to be 0.86.

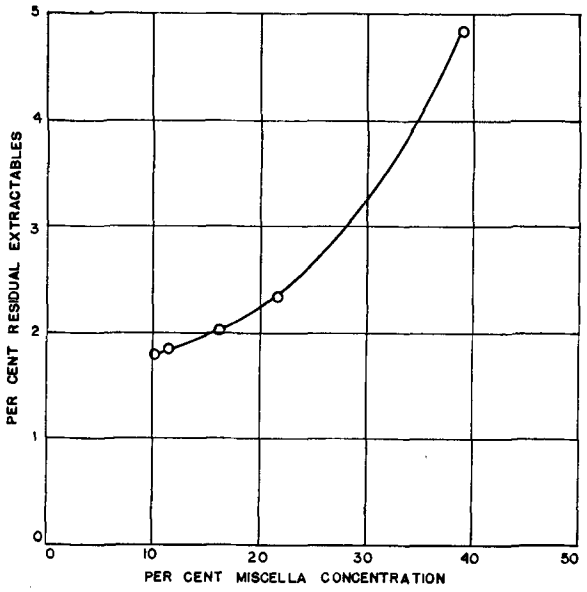

FIG. 4. Effect of miscella concentration on residual extractables in pilot plant.
Extraction temperature, 110°F. Extraction time 26.5 minutes. Moisture 4.7 to 5.5%. Extractables calculated to moisture-free basis.

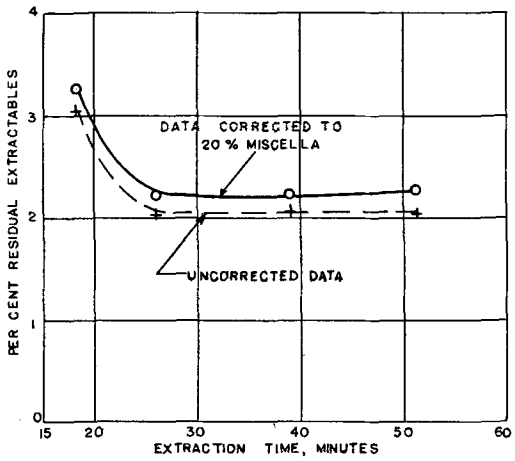

FIG. 5. Variation of residual extractables with extraction time in pilot plant.
Extraction temperature, 110°F. Moisture content 4.7 to 5.1%. Extractables calculated to moisture-free basis.

Meat and bone scrap is rendered meat, and, as a result, most of the fat has diffused to the surface of the protein particles. The process of solvent extraction of this material is then primarily an operation of washing off the fat from the particles with little opportunity or need for diffusion from the interior to take place. The data shown in Figure 5 confirm the extraction process as being one of washing from the surface rather than one of diffusion from the interior since extraction periods in excess of 25 minutes do not aid the removal of the fat. This washing process theory is supported by the fact that miscella concentrations along the horizontal section of the pilot

plant extractor did not change appreciably, being of the order of 2 to 4% fat. This portion of the extractor represents about 48% of the extraction zone. It has also been observed in this section that the meat and bone scrap and miscella form three distinct phases. The phase at the top of the confining conduit is the meat portion of the feed, at the bottom are the bones, and between these is a layer of clear miscella. A passage is thereby presented which permits the extracting media to bypass most of the material being extracted. It can nevertheless be argued that during the period that the meat and bone scrap is traversing the horizontal section, since it is immersed in miscella, diffusion could be taking place. This should result in a reduction in the residual extractables since the material is washed with pure solvent as it leaves the extraction zone. Since a reduction within experimental error does not occur, diffusion, if present, must be slow.

The upward trend in the residual extractables at extraction times below 25 minutes is explainable in part on the basis that as the chain speed increases, a greater amount of frictional drag is imposed upon the meat and bone scrap. This drag packs the material so that free washing of the meat particles does not readily occur.

The effect of temperature on laboratory rate extraction shown in Figure 6 is that normally found in

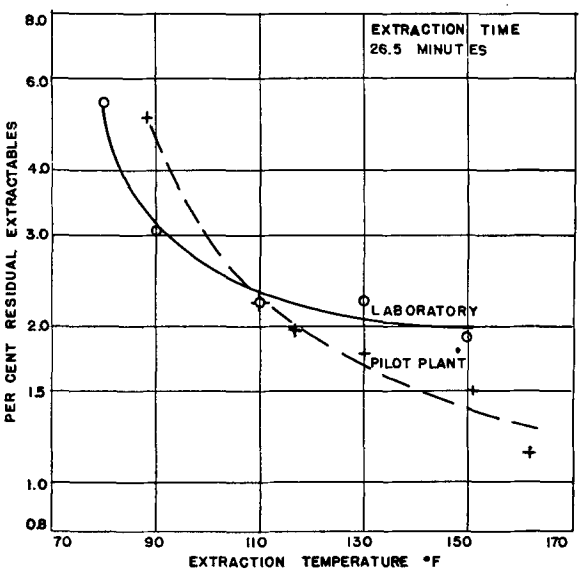

FIG. 6. Comparison of laboratory and pilot plant data on meat offal with constant extraction time.

solvent-extraction studies. The data for pilot plant extractions on the same material are included on the same figure so that a comparison of the effect of temperature on laboratory and pilot plant scale can be made. The difference in the effect of temperature is the result of the differing effects of temperature on the density of the extracting solution. In a solution possessing a specific gravity of 1.30 it was found that the non-bone portion of the meat and bone scrap would separate into about two equal portions. In lower specific gravity solutions all of the material was at the top of the solution. In the case of laboratory rate extractions the specific gravity of the solution is close to that of pure solvent and is never much less

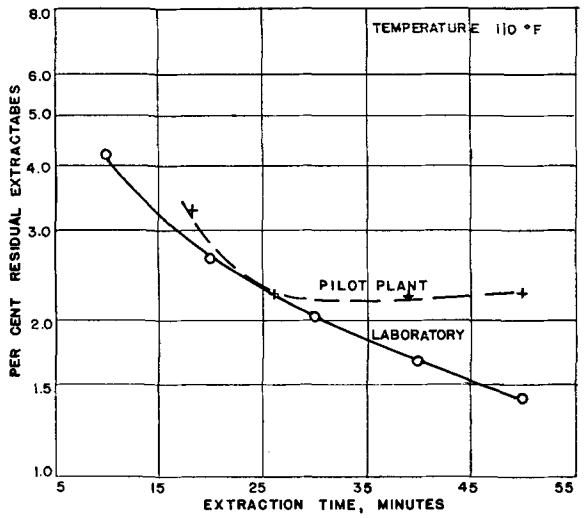

FIG. 7. Comparison of laboratory and pilot plant data on meat offal with constant extraction temperature.

than 1.38 so that the material always rides at the top of the solution. Therefore the extraction takes place through a static bed which is almost constant as far as packing is concerned, and this packing is independent of temperature. For pilot plant extractions the solution is not pure solvent but an oil-solvent mixture, and, in addition, a drag is imposed on the material by conveyor flights which aggravates the packing tendencies. At low temperatures the material rides at the top of the conduit because the miscella specific gravity is above that of the meat particles, but as the temperature is increased, the miscella specific gravity decreases and may fall below that of the solids. It is therefore probable that as the temperature is increased, the packing of the bed being extracted in the pilot plant is decreased and the washing process is improved, thus increasing the efficiency of extraction.

With an extraction temperature of 150°F. and an extraction time of 26.5 minutes, it was found that it was possible to obtain extraction efficiencies as high as 98.3%. The moisture content of the feed material was 5.0%.

The data given in Table II show that the solvent trichloroethylene is the preferred solvent since, for a given extraction time, it removes a greater percentage of the soluble components.

Comparison of Laboratory and Pilot Plant Results

In all solvent extraction work it is desirable to obtain some correlation between laboratory and pilot plant extraction. This correlation is made more difficult because the extracting solutions differ considerably in physical properties. Also one extraction process is static in nature whereas the other is dynamic. There also enters the problem of being able to define the mechanism whereby the extraction takes place.

In an effort to find a correlation between laboratory and pilot plant data, the meat and bone scrap used in the pilot plant investigation was subjected to the rate extraction procedure. A potential correlation between the two extraction procedures is shown in Figures 6 and 7. These figures show that if data for the effect of extraction time for both laboratory and pilot plant experiments are plotted on the same figure

with constant temperature, and data for the effect of extraction temperature are plotted at constant extraction time, the curves cross or touch at the same location. With meat and bone scrap this coincidence occurs at an extraction time of 26 minutes and an extraction temperature of 110°F. This extraction time is the one commonly used in the commercial Iowa State College extractor, and the temperature is that normally used in the laboratory study of many materials. This correlation means that with meat and bone scrap one can estimate the residual extractables obtainable in the pilot plant by making a single laboratory rate extraction.

This empirical approach did not prove to be satisfactory for cottonseed, but this can be explained on the basis of a difference in mechanism. Solvent extraction of meat and bone scrap takes place mainly by a washing process whereas it is believed (5) that with cottonseed it is a diffusional operation.

The toxicity to cattle of certain batches of trichloroethylene-extracted soybean oil meal has raised the question of possible toxicity of other products extracted by trichloroethylene. Since the work presented in this paper was a study in extraction only, the use of trichloroethylene as an experimental solvent should not be construed as a recommendation by the authors that the product resulting from this extraction is or is not suitable as a feed.

Summary

Data are presented to show the effect of the various operating variables on the extraction of meat and bone scrap both in the laboratory and in a pilot plant model of the Iowa State College extractor. From the data presented it has been concluded that the extraction takes place mainly by a washing process with slight diffusion. A possible correlation is suggested for comparing laboratory and pilot plant data.

REFERENCES

1. Arnold, L. K., and Juhl, W. G., J. Am. Oil Chemists' Soc. (in press).
2. Arnold, L. K., and Patel, D. J., J. Am. Oil Chemists' Soc., *30*, 216-218 (1953).
3. Arnold, L. K., and P'Pool, R. S., J. Am. Oil Chemists' Soc., *30*, 611-613 (1953).
4. Arnold, L. K., Sweeney, O. R., and Russell, R. F., J. Am. Oil Chemists' Soc., *30*, 393-396 (1953).
5. Karnofsky, George, J. Am. Oil Chemists' Soc., *26*, 564-569 (1949).
6. Sweeney, O. R., and Arnold, L. K., J. Am. Oil Chemists' Soc., *26*, 697-700 (1949).

[Received April 20, 1954]

A Modification of the p-Anisidine Method for the Determination of Free and Total Gossypol[1]

W. J. MILLER, The Buckeye Cotton Oil Company, Atlanta, Georgia

A modification of the Pons and Guthrie[1] method for the determination of free gossypol and the Pons[5] method for total gossypol in cottonseed materials is presented. The proposed procedure makes possible the analysis of free and total gossypol in chemically treated products containing dianilinogossypol. The methods presented are spectrophotometric ones in which dianilinogossypol is formed as a measure of the free or total gossypol. The free gossypol method is applicable to the analysis of all types of cottonseed meals available commercially. The advantage of the modified methods is that accurate results can be obtained when the sample contains dianilinogossypol.

The method of Pons and Guthrie for the determination of free gossypol in cottonseed materials is an Official Method of The American Oil Chemists' Society. The total gossypol method has no such official standing. However both have been generally accepted as the most satisfactory methods available.

Neither has previously been evaluated completely with regard to its applicability to materials that have been chemically treated to reduce their free gossypol content. The object of this work was to examine the methods thoroughly with respect to the analysis of cottonseed materials containing dianilinogossypol. Since dianilinogossypol is physiologically inert, it is important that this material not analyze as free gossypol when present in cottonseed meal. It is important, too, that the dianilinogossypol be completely hydrolyzed in the total gossypol method.

Briefly the free gossypol method of Pons and Guthrie requires the ground sample to be extracted with 70% aqueous acetone, using a mechanical shaking device. An aliquot of the acetone solution of gossypol is then allowed to react with p-anisidine, in the presence of acetic acid, for 30 min. at 60° C. A solution of the yellow gossypol-anisidine complex, in alcohol, is measured with a spectrophotometer or a photoelectric colorimeter at 447 mu. Pons' total gossypol method requires the hydrolysis of combined gossypol by oxalic acid in a solution of methyl ethyl ketone-water azeotrope. The liberated gossypol is then measured as in the free gossypol method.

[1] Presented at 45th annual meeting, American Oil Chemists' Society, San Antonio, Tex., Apr. 12-14, 1954.

Discussion

Correlation between feeding tests, using meals containing dianilinogossypol, and free gossypol measurements made by the Official Method have indicated that the method tends to give high results. This was not the case when studying untreated meals. It is likely that dianilinogossypol is extracted along with the free gossypol and that its presence is not entirely corrected for since its extinction coefficient is different from that of the anisidine complex, at 447 mu. It will be shown later that this is only a partial explanation.

Using pure dianilinogossypol, it was shown that it is extracted, to some extent, without hydrolyzing, with 70% aqueous acetone, under the conditions of the test. Reaction with p-anisidine resulted in the measurement of apparent free gossypol.

A study of other solvents was made in the hope that the extraction of dianilinogossypol could be eliminated. This work was unsuccessful. None was as effective as 70% acetone in extracting free gossypol. The stability and solubility of gossypol in aqueous acetone, as pointed out by Pons and Guthrie, make it the most desirable solvent that could be found.