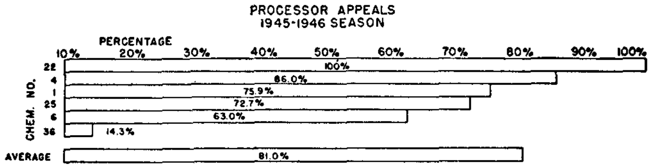
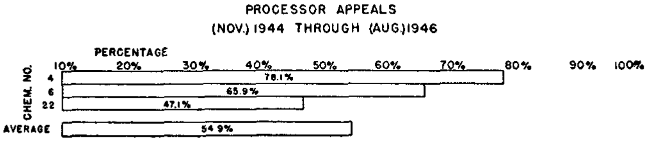


PERCENTAGE OF ORIGINAL ANALYSES SUSTAINED ON SAMPLES CALLED FOR APPEAL ON WORK OF VARIOUS APPROVED CHEMISTS BY PROCESSORS

FIG. 10.



PERCENTAGE OF ORIGINAL ANALYSES SUSTAINED ON WORK OF APPROVED CHEMISTS ON WHOM APPEALS WERE CALLED BY PROCESSORS DURING BOTH SEASONS AS INDICATED.

FIG. 11.

In addition this figure shows the final grade obtained by each chemist on the required series of check samples sent out weekly by the Memphis office of CCC for further checking on the approved chemists' work on analyses.

Upon careful examination and analysis of the percentages shown on each of the accompanying figures, Nos. 1 through 12, it will be seen that the *best all-around* record of all the approved chemists was made and maintained throughout both seasons by the chemist identified as No. 2, who is a processor chemist. He was checked more closely and frequently by each of the referee chemists than was any other approved chemist. This applies to both check samples sent in and to appeal samples involved in appeals requested by CCC and processors. Of the several referee chemists used by the Memphis office for both check and appeal analyses, chemist identified as *No. 4,* a commercial chemist, made and maintained the *best all-around record* and is second only to chemist No. 2.

It is believed that the analytical work as performed by the approved soybean chemists during the period of November, 1944, through September, 1946, resulted in a marked improvement in the application of the technical methods of analysis and in the accuracy of the results obtained and is an indication of what may be accomplished by special precautions to improve the quality of laboratory work. It is also believed that the analytical procedures and accuracy of results can be further improved, and that additional studies will result in better methods of analysis and the use of better equipment and techniques by chemists.

The writer would like to express his appreciation for the sound advice and the timely suggestions of the advisory committee of the American Oil Chemists' Society during the two years that the supervision work of soybean analysis was assigned to the Memphis office (Messrs. S. O. Sorensen, N. F. Kruse, V. C. Mehlenbacher, E. C. Ainslie, representing the soybean industry; Messrs. G. W. Agee, N. C. Hamner, Thomas C. Law, E. H. Tenent, representing the approved commercial chemists; Messrs. R. T. Milner, T. H. Hopper, G. S. Meloy, representing the government), as well as many of the approved chemists, both industrial and commercial, with whom he conferred.

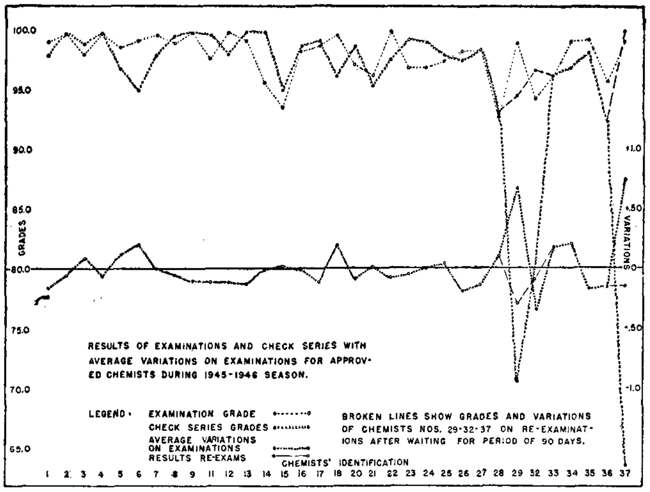


FIG. 12.

Report of Gossypol Committee[1]

TENTATIVE conclusions and recommendations are herewith presented concerning the different published methods for extraction and estimation of gossypol in cottonseed which were investigated by the Gossypol Committee.

Summary of the Program of Investigation Completed by the Gossypol Committee

Two samples of pure-bred (homogeneous) prime cottonseed were sent to all of the members, and simultaneous tests were carried out on these samples. Several different methods for the estimation of gossypol were applied to aliquots of each extract prepared by different methods so that the methods of extraction and estimation were tested independently of each other. Each member submitted a detailed report of his results and conclusions to the Chairman. On the basis of these individual reports a committee report was drawn up and submitted along with copies of the individual reports to each member of the committee.

Conclusions and Recommendations[2]

A. PREPARATION OF SAMPLES.

1. The wide variation in values obtained by different investigators, coupled with the relatively consistent results of each investigator, indicates the probability of sampling errors. This appears to be attributable to differences in methods of preparation of the samples. (Five.)

2. For preparation of large samples of meats, flaking appears to be the best method of obtaining exposure of the pigment glands without undue heating of seed and consequent alteration of some of the gossypol. (Four.)

3. For the preparation of small samples of meats, as for application of spectrophotometric methods of analysis, the following method is recommended. A relatively large sample, about 100 g., of coarsely ground or flaked meats is mixed and quartered. Then

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[1] Previous report, Oil & Soap, 23, 235-236 (1946).

[2] The figure in parentheses after each recommendation or conclusion indicates the number of members (total number, 5) agreeing with the recommendation or conclusion which the figure follows.

a smaller sample is finely ground in a glass mortar, and extracts are prepared from weighed amounts of the finely ground meats. (Five.)

4. For the sake of comparison of results, the gossypol content should be expressed in terms of hull-free kernels. (Five.)

B. Methods of Extraction of Gossypol From Cottonseed.

1. Exhaustive extraction of cottonseed with diethyl ether refluxed on a steam bath (1, 2, 3) yielded low values because of decomposition of gossypol upon its prolonged contact with diethyl ether at elevated temperatures. (Four.)

2. Initial use of a mixture of peroxide-free diethyl ether, ethanol, and water (2) yielded somewhat higher values for gossypol, but they were lower than those obtained with the equilibration and blending methods. (Five.)

3. Less prolonged extraction with the above-mentioned methods (1, 2, 3) also yielded low values for gossypol. (Five.)

4. Equilibration of ground or flaked meats with diethyl ether or chloroform at 38° F. (4) yielded complete extraction of gossypol in 24 hours. (Five.)

5. Equilibration of ground or flaked meats with chloroform at room temperature with constant agitation (5) yielded complete extraction in less than 24 hours and decomposition of the extracted gossypol after about six hours. (Five.)

6. The methods for the extraction of gossypol with the use of aqueous ethanol mixtures (6, 7) were not satisfactory in all cases, but the poor results appeared to be due to difficulties in manipulation. Both methods are difficult to carry out quantitatively, but because of their speed they would appear to be the most desirable methods for the extraction of gossypol. (Four.)

Two of the members urgently recommended elimination of the use of diethyl ether in the Blendor method of F. H. Smith (7).

C. Methods of Estimation of Gossypol in Cottonseed Extracts.

1. The gravimetric methods tested (1, 8, 9) were equivalent to the spectrophotometric methods (3, 4, 7) in some cases, lower in others. However, decomposition of gossypol during its extraction with diethyl ether refluxed on a steam bath vitiated results. (Five.)

2. The three spectrophotometric methods investigated (3, 4, 7) were found to be approximately equivalent by different investigators, but some difficulty was experienced with each method. Each method appeared to require some modification, or at least further re-checking in order to establish its specificity and reproducibility. (Five.)

3. Because of the narrowness of the dianilinogossypol absorption band, low dispersion instruments such as the Coleman spectrophotometer cannot be employed for obtaining accurate results. (Two.)

4. Standardization of dianilinogossypol formed from pure gossypol in the solvent mixture, ethanol, water, and diethyl ether, according to the method of F. H. Smith (7) did not yield reproducible results in the hands of different investigators. This may have been due to the failure to add glacial acetic acid as later recommended by F. H. Smith (10), but it appears more likely to have resulted from the use of mixed solvents and subsequent prolonged heating so that the final proportions of solvents may have varied widely. Future investigations of this method should be directed toward avoiding the use of mixed solvents. (Three.)

5. Investigations of the dianilinogossypol-spectrophotometric method of Lyman, Holland, and Hale (3) indicated some variation in the time necessary for completion of the reaction in the case of cottonseed extracts. Future investigations of this method should be directed toward redetermining the minimum average period for completion of reaction with various extracts. (Three.)

6. The antimony trichloride-spectrophotometric method for gossypol (4) gave difficulty because of the sensitivity of the reagent to moisture and the short period of time during which readings specific for gossypol can be obtained. Since these difficulties are inherent in the reagent, general adoption of the method will depend upon whether the accuracy of the method is believed to compensate for the difficuty involved in applying it. (Five.)

D. Specificity of Methods of Estimation.

1. Investigations of the specificity of the various proposed methods for the estimation of gossypol in cottonseed extracts were not conclusive. (Five.)

2. Future investigations should employ the recently developed method for the quantitative extraction of gossypol from cottonseed extracts by use of aqueous alkali (11). This method permits isolation of the acidic gossypol from accompanying non-acidic components of cottonseed extracts. Comparison of results obtained by application of a given method to the isolated gossypol and to the extract will permit determination of the specificity of the method. (Three.)

3. If necessary, the alkaline extraction method can be incorporated as part of the method adopted. (Two.)

E. Pure Gossypol for Standardization.

1. One of the members of the committee, F. H. Smith, reported that after several months the pure gossypol (12) which had been furnished to the committee for standardization of the various spectrophotometric methods yielded lower values with the dianilinogossypol method (7) than some gossypol which he had prepared (13). Re-testing of the standard gossypol by the antimony trichloride-spectrophotometric method demonstrated that the gossypol had deteriorated since it had first been prepared.

2. It will be necessary to establish methods for the preparation and preservation of pure gossypol, or alternatively, to establish standard reference values for pure gossypol for the method adopted. It is suggested however, that committee action in this matter should not be taken until more data concerning the properties of pure gossypol have been published or made available. (Five.)

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C. M. Lyman
H. D. Royce
Allen Smith
F. H. Smith
Charlotte H. Boatner,
chairman.

The Measurement of the Hydrolysis of Solutions of Sodium Salts of Fatty Acids. I.

J. W. McBAIN and ANDREW VAN TUYL
Department of Chemistry
Stanford University, California

Introduction

THERE are two main problems in the study of the hydrolysis of soap solutions. The first is to establish the extent to which soaps are hydrolyzed in solutions under various conditions; and estimates have ranged from negligible amounts to 100% (1, 2). The second problem is to ascertain the products of hydrolysis. These have been variously assumed by different workers to be free fatty acid and free alkali, acid soaps of fixed or variable composition, and basic soaps.

The concept arrived at by McBain and his collaborators was that hydrolysis, though always present, yielding distinctly alkaline solutions even in the presence of excess fatty acid, is of minor extent except in the most dilute solutions. Of course, such dilute solutions are of importance in washing processes, and particularly in rinsing. The products of hydrolysis are taken as hydroxyl ion and one or more acid soaps of such composition as NaP:HP and 2NaP:HP, where P stands for a soap radical such as palmitate. Basic soaps are thought not to exist and free fatty acid is present only in extremely small amount, never enough even to equal its low solubility in water. Hence solid or liquid free fatty acid never separates out from soap solutions unless these are decomposed by carbonic acid or other acid.

In contrast some have assumed, without direct evidence, that free fatty acid as such is present in excess at all concentrations of soap solution. Ekwall (18) considers that this is only true in extreme dilution and Powney and Jordan (16) considered it untrue for dilute solutions and for concentrated solutions, but that free acid is present as such only in a range of moderate dilution.

Soaps were first studied extensively in 1823 by Chevreul (3); and in connection with the study of hydrolysis it was the investigation of the acid soaps deposited in dilute solutions with which he was concerned. Krafft from 1894 onwards studied the same phenomena (4).

In 1914 McBain and Martin measured the true hydrolytic alkalinity of pure soap solutions at 90° C. by means of the hydrogen electrode (1). The results of these experiments were confirmed by experiments of other kinds. McBain and Bolam in 1918 compared the catalytic effect of soap solutions on the decomposition of nitrosotriacetoneamine with those of known solutions of sodium hydroxide (5). McBain and Jenkins used the ultrafilter (6), McBain and Buckingham in 1927 (7) and McBain and Eaton in 1928 (8), measured the concentration of fatty acid in soap solutions by means of distribution experiments with non-aqueous solvents, and calculated the alkalinity. McBain, DuBois, and Hay in 1926 found the indicator method applicable to solutions of higher concentrations (9).

These experiments were interpreted in the light of the theory of colloidal electrolytes developed by McBain and set down in detail in 1920 in a paper by McBain and Salmon (10).

In 1927 McBain and Stewart prepared crystals of acid potassium oleate of the composition KOl: HOl from alcoholic solution (11). A large number of crystalline acid soaps have since been prepared by Ekwall and others (12), and in most cases conclusions from the results of analyses, melting point determinations, and x-ray studies (13) were that the acid soaps actually exist as crystalline compounds. Phase diagrams of various soap systems were studied by McBain and Field in 1933 (14). Ekwall in 1938 used a microscope equipped with a hot stage to examine the crystalline material suspended in soap solutions at different concentrations and temperatures, also analyzing the sediments (15).

The measurement of the degree of hydrolysis of soap solutions was taken up systematically in 1938 when Powney and Jordan obtained hydrolysis-concentration curves using the glass electrode (16) and when Stauff used the hydrogen electrode (17). Stauff used the curves as the basis of a new theory of hydrolysis which assumed association of fatty acid anions and hydrolysis of the associated anions to give the acid soap. This theory was made more extensive and complete by Ekwall in 1940 (18) who considered that it explained the hydrolysis-concentration curves he obtained for sodium laurate (19) and sodium caprate at 20° C. (20).

The present paper is concerned with the titration of acetic, lauric, and myristic acids in alcohol and in water; a later communication will record the pH values of a series of soap solutions at 25° C., the solubility of the higher fatty acids in water, and the extent to which all the aqueous soap solutions are unsaturated with regard to fatty acid.

Experiment and Discussion

Measurement of the pH of aqueous sodium acetate. First, decinormal solutions of Baker's Analyzed and of Kahlbaum's sodium acetate were prepared using boiled-out conductivity water, and they were found to