fold effect: economic and hygienic. The first involves the substitution of a cheaper though perhaps just as wholesome a substance, the removal of a valuable ingredient, the addition of something affecting strength or quality or the concealment of damage or inferiority by coloring, coating or powdering. The second considers the question of injury to the public health. Such is the case of filthy, decomposed or putrid animal or vegetable matter, or of added poisonous or harmful ingredients or of the product of a diseased animal or one that has died other than by slaughter. In the first class of cases, the consumer's health need not be concerned.

A drug is deemed adulterated if it fails to conform to the specifications of the U. S. Pharmacopeia and the National Formulary, unless a deviation from standard is declared on the label. Certain substances are banned from use in confectionery such as minerals, narcotics, poisonous colors or flavors, etc. A mere chemical trace is sufficient to condemn the product. If the normal strength of an article is reduced or diluted or if an ingredient normally present is found to be absent, adulteration exists. In the case of food products prepared for shipment by the external application of some preserving agent, containing harmful substances, which can however be removed mechanically or by macerating with water, as for example sprayed fruits and vegetables, the provision of the Act regarding added poison, etc., applies only when such products are ready for consumption.

Food need not be harmful at the time of seizure. It is enough that it can be proved to become so within a reasonable time. Nor does the government have to prove it must affect public health; it is adulterated if it may injure anybody. Human intervention likewise is unnecessary. Whether a food is naturally putrid or becomes so by accident, the Act still applies.

For accurate ascertainment of misbranding and adulteration, there must be suitable standards for comparison. No analyst can pass intelligently on samples collected in suspected cases of violations without a knowledge of the true composition of the products they purport to be. Hence the scientific staff of the Food and Drug Administration is constantly engaged in investigation and analysis, and their results in specific cases will indicate when prosecution lies, and become in the ensuing litigation the vital evidence for conviction. The chemist is therefore a prime factor in the establishment of the necessary standards, in the interpretation of merchantability, wholesomeness, misbranding and adulteration, without which the courts cannot proceed to render a just decision.

COMPARISON OF TWO METHODS FOR THE DETERMINATION OF CONJUGATED DOUBLE BONDS

By K. A. PELIKAN, Ph. D., and J. D. von MIKUSCH, Ph. D.

WOBURN DEGREASING COMPANY OF N. J.,
CHEMICAL DIVISION, HARRISON, N. J.

EARLY in 1936 H. P. Kaufmann and J. Baltes[1] published a laboratory method to determine the number of conjugated double bonds in oils and fatty acids which they expressed in equivalents of iodine and called the "Diene Value."

> The weighed sample is dissolved in acetone and a known excess of maleic anhydride is added. This solution, contained in a sealed tube, is kept in an oven at 100° C. for 20 hours. After cooling, the solution is poured into water and an emulsion forms, which breaks after several hours. Finally, the maleic acid in the water solution is titrated with N/10 alkali after separating it from the oily layer by filtration.

Later, a similar method was suggested by B. A. Ellis and R. A. Jones,[2] requiring considerably less time and which they claim is "more on practical lines."

> In their directions toluene is used as solvent and the solution is refluxed for 3 hours or—after adding a small amount of iodine as catalyst—for 1 hour. After hydrolizing, ether is added and the excess maleic acid washed out in a separatory funnel for titration. A larger sample and normal alkali solution is used in this method.

While both groups of investigators have obtained approximately the same value of 70 for tung oil, and the theoretical value of 87 for β-elaeostearine, K. and B. have also tested their method successfully with anthracene and Δ9,11-linolic acid. Among the samples analyzed by E. and J. was one of "medicinal castor oil" for which they found the Maleic Value of 10.5.

Though E. and J. suggest the name "Maleic Value" for the new constant rather than "Diene Value," as preferred by K. and B., both values are calculated in the same manner in terms of iodine and should be identical.

As the Ellis method requires much less time it seemed advisable to compare the results of the two methods and if they should disagree to ascertain which one represents the amount of conjugated double bonds more correctly. The statement by E. and J. that: "This method (Kaufmann method) is not well adapted for general application, and the results recorded would seem to be subject to variations of considerable magnitude," calls for correction in as much as we had used this method for a number of determinations during the last year and could not complain of any considerable variations. In fact, we usually checked our results within a few tenths of a point. Though the long reaction time, requiring the leaving of the samples in the oven over night, was felt to be a handicap we never objected to the use of small quantities of a few tenths of a gram which is of the same magnitude as that used for iodine numbers and other determinations. Thus we can see no advantage in the use of samples of 3 or more grams in the Ellis method. The use of normal alkali as opposed to the more dilute solution needed for the Kaufmann method was also of no advantage in our case as standardized N/6 alcoholic KOH is used in our laboratory for acid number

[1]Fette und Seifen 43, 6-7, 93 (1936).
[2]Analyst 61, 812-6 (1936).

determinations and is always ready for use.

Experimental data

In comparing the two methods, we at first used samples of commercially dehydrated castor oil containing an unknown amount of Δ9,11—linolic acid. The Kaufmann method was employed with the single variation that the maleic acid was titrated with N/6 alcoholic KOH instead of with N/10 aqueous NaOH. The oven temperature could not be controlled any better than about ±5° C. In carrying out the Ellis method we followed the instructions given for the short time variation (in presence of iodine) since equal accuracy is claimed for both variations. However, instead of using a spiral condensor we were satisfied with a straight air condensor with ground connection to the flask after ascertaining by a number of blank runs that no appreciable amounts of maleic anhydride were lost in this procedure (Table 1). The toluene as well as the acetone used was Baker's c. p.; the maleic anhydride was the same in both cases.

TABLE 1—Blank Runs with Different Periods of Refluxing (Ellis Method)

Date	Apr. 5, '37	Apr. 6, '37	
ml KOH consumed..	28.53	....	No refluxing, hydrolized in separatory funnel.
	28.53	28.50	Refluxed directly with H_2O 15 minutes.
	28.30	28.40	Refluxed 1 hour before adding water.

In order to compare not only the methods directly but at the same time the dependence of the results upon minor factors, such as the weight of the samples, the latter were allowed to vary about 100% in the duplicates; also the period of heating was varied about 100% in one of the determinations by the Kaufmann method. The following table shows the results:

It will be noted that the values obtained by the two methods disagree considerably (up to 50%), the Ellis method giving the higher results. Furthermore, in both cases the results depend on the weights of sample used, though this variation is considerably greater in the Ellis method.

A sample was then tested which could not possibly contain any conjugated double bonds. We suspected that the higher values obtained with the Ellis methods might be caused by the presence of hydroxy acids or their esters in some of the investigated samples (the value of 10.5 for medicinal castor oil for instance which E. and J. found seems unusually high). We therefore used hydrogenated castor oil with an iodine number of 1.2 for this test.

The maleic value obtained by the Ellis method in this case obviously cannot represent any double bonds. Apparently, some maleic anhydride reacts in a different way than the Diene-synthesis of Diels and Alder[3]). Probably a reaction with hydroxyl groups takes place similar to an acetylization. We have not identified the reaction product formed, but we were able to show that the maleic anhydride has actually reacted with the oil and has not just been lost through experimental conditions: We thoroughly washed the product obtained in a parallel run, (similar in all details to the Ellis procedure) with hot water until the last traces of maleic acid were removed as shown by neutrality to methyl-orange. The saponification number of the product then was 192.5 as compared with 180.6 for the untreated hydrogenated castor oil. This increase of 11.9 in the sap. number corresponds to a maleic value of about 3.4; a fairly good agreement with the results shown in Table 3.

[3]Annalen **460**, 98 (1928).

TABLE 3—Comparison on Hydrogenated Castor Oil, Iodine Number = 1.2

Ellis Method		Kaufmann Method	
Wght. of Samples	Maleic Value	Wght. of Samples	Diene Value
6.299	4.2	1.904	0.23
10.225	3.9		

TABLE 2—Comparison of Both Methods with Duplicates of Varying Weights of Sample

Material	Ellis Method Wght. of Sample	Maleic Values	Diff.	Kaufmann Method Wght. of Sample	Diene Values	Diff.	Discrepancy between the methods
Dehydrated Castor Oil...	3.001	20.8	2.6	0.3167	14.1	1.1	
Dehydrated Castor Oil...	5.999	18.2		0.5892	13.0		
Average	....	19.5		.....	13.6		5.9
Distilled Fatty Acids from Dehydrated and Split Castor Oil	3.019	26.8	5.5	0.2553	16.8*	1.4	
	6.020	21.3		0.5158	15.4**		
Average	....	24.1		.....	16.1		8.0

*In oven at 95-100° C. for 40 hrs. **In oven at 95-100° C. for 21 hrs.

Conclusions

Our analytical data show that with certain compounds the Ellis method gives too high results. They also show that the results obtained by the Ellis method depend to a greater extent upon the weight of sample used than those found by the Kaufmann method. No indications have been observed in these experiments as well as in other routine determinations to support the statement that the Kaufmann method is unreliable.[4] However, a need is felt for a method which would combine the greater reliability of the Kaufmann method with the greater speed of the Ellis method.

No reason can be seen for renaming the original method after a few changes. Priority rights are due to H. P. Kaufmann and his co-workers. His "Diene Value" indicates exactly the quantitive evaluation of conjugated double bonds.

[4]Berichted d.D. Chem. Ges. **70**, 900, 903, 908 (1937).

REPORT OF REFEREE BOARD

The activities of the Referee Board for the past year included the usual appointment of Referee Chemists and distribution of 10 cottonseed samples and 5 crude cottonseed oil samples for collaborative test by the Referee Chemists and voluntary collaborators.

Thirty-three Referee Certificates were issued. The names of the Referee Chemists were published in OIL AND SOAP and need not be reproduced in the present report.

The average standard of work of our Referee Chemists is believed to be even higher than formerly. Most of the credit for this must be given to the efforts of the Referee Chemists themselves, but there are definite indications that the activities of the Referee Board in connection with the collaborative samples, including the check meal samples of the Smalley Foundation Committee, have had a beneficial effect. The committee's only recommendation is that the collaborative test samples be continued, and all the collaborators are invited to offer constructive criticism for improvement of the program.

J. P. HARRIS
N. C. HAMNER
E. C. AINSLIE
J. J. VOLLERTSEN
A. S. RICHARDSON
Chairman.