A Useful Constant for Oil Identification

The Use of the Kaufmann Thiocyanogen Value in The Analysis of Fats and Oils[1]

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IT HAS been known for a long time that certain organic and inorganic radicals have the properties of elements. The most familiar example is probably the ammonium group (NH_4) which acts as though it were an alkali metal. Nearly 100 years ago, Berzelius, as the result of a study of the salts of thiocyanic acid, predicted that if the radical thiocyanogen (SCN) could ever be isolated in the free state, it would be found to have many of the properties of a halogen.

Several unsuccessful attempts were made to prepare this substance, but it was not until about 15 years ago that the Danish chemist Bjerrum succeeded in demonstrating the presence of free thiocyanogen in the mixture of decompostion products of gold thiocyanate in aqueous solution. He found the substance to be very unstable, in aqueous solution rapidly undergoing hydrolysis with the formation of thiocyanic, hydrocyanic and sulphuric acids.

In 1919, Söderbäck isolated thiocyanogen in pure form, and published an extensive study of its properties and reactions. The substance was prepared by the action of bromine on silver or lead thiocyanate suspended in ether or other organic solvents. The properties of thiocyanogen strikingly verify the prediction of Berzelius. It liberates iodine from iodides, dissolves metals, even gold, with the formation of thiocyanate: is a powerful oxidizing agent and generally possesses all the characteristics of a halogen intermediate in chemical activity between bromine and iodine. Kaufmann, in 1921, was attracted to thiocyanogen by the need for a halogen reagent which would react less strongly than bromine but more strongly than iodine. His success with the reagent in other organic researches suggested the possibility of using it in fat analysis as a means of differentiating the various unsaturated fatty acids.

A careful investigation of the action of thiocyanogen on saturated and unsaturated acids showed the following results.

Saturated acids, would be expected, do not react.

Oleic acid adds thiocyanogen in the same proportion as iodine: i.e. molecule for molecule.

Linolic acid adds thiocyanogen to only *one* of its two double bonds, while iodine is added to both. Thus linolic acid has an iodine number of approximately 180, while its "Kaufmann number" is only 90, the same as for oleic acid.

Stearolic acid, with a triple bond, does not add thiocyanogen.

Analytical Use

THE peculiar behavior of linolic acid at once suggested the possibility of using this value in the analysis of such fats as lard, tallow, cottonseed or peanut oil etc. containing no acids less saturated than linolic. The departure of the thiocyanogen number from 90 gives a measure of the saturated acid fraction, while the difference between the iodine and Kaufmann number gives the linolic acid content.

Recently, Kaufmann and Keller have extended the method to the estimation of the linolenic acid in drying oils. Linolic acid adds thiocyanogen to two of its three double bonds, and if the saturated acid content is separately estimated by the Twitchell or Bertram methods, the linolenic acid content can be calculated from the iodine and thiocyanogen numbers.

The estimation of the Kaufmann numbers is very easily carried out. The reagent is prepared by suspending dry lead thiocyanate in anhydrous acetic acid, decomposing with dry bromine, and filtering. Lead thiocyanate is easily prepared in the laboratory from lead acetate and postassium thio-

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cyanate: anhydrous acetic acid is made by refluxing C. P. glacial acetic acid with a slight excess of acetic anhydride. Kaufmann recommends N/1o solutions; we have found it convenient to use N/5, since larger fat samples can be used and greater accuracy obtained. All the reagents and apparatus used, including the fat sample, must be thoroughly dry. The solution is stable for about one week. The technique of the determination is identical with that for the Wijs iodine number estimation. A solvent for the fat or fatty acid is unnecessary. The reaction is slower than the absorption of iodine, but is complete on standing over night. The thiocyanogen absorption is expressed in terms of iodine.

Comparative Analyses

IN ORDER to investigate the possibility of using this method for plant control of hydrogenation, we undertook the analysis of two series of samples of cottonseed oil drawn at various stages in the hydrogenation process. The samples were analysed by the Kaufmann method and also by the Twitchell lead salt-alcohol method. The results of the first series are shown in table 1.

TABLE I

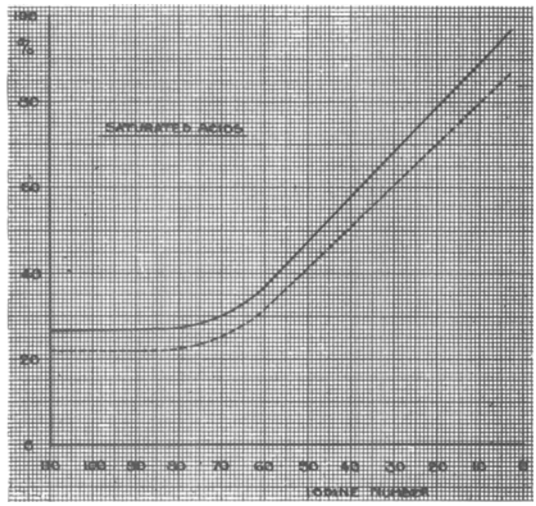
Sample No.:	Iodine Number	Kaufmann Number	Saturated acids %	Linolic acid %
1	107.2	65.6	27.1(22.6)	46.2(41.7)
2	97.2	65.9	26.8(22.8)	34.8(28.8)
3	91.0	65.2	27.6(22.1)	28.7(20.8)
4	84.0	65.9	26.8(24.9)	20.1(16.0)
5	79.7	65.9	26.8(25.4)	15.3(11.7)
6	75.8	66.2	26.5(26.6)	10.6(7.9)
7	75.6	66.3	26.4(26.0)	10.2(7.7)

The second series is more extensive, the hydrogenation being carried to completion. These results are shown in table II.

TABLE II

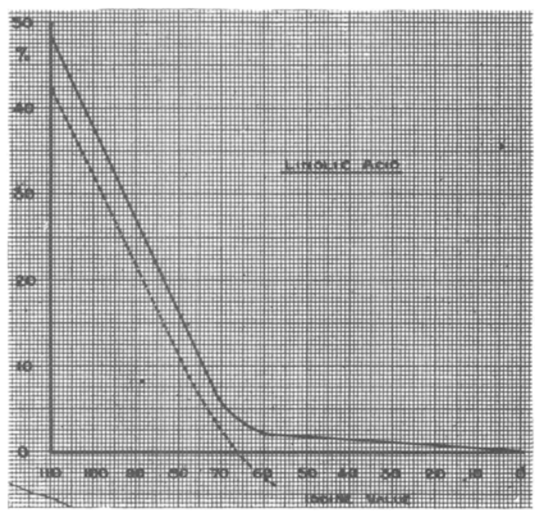
Sample No.:	Iodine Number	Kaufmann Number	Saturated acids %	Linolic acid %
1	109.4	66.2	26.4(21.2)	48.0(42.1)
2	94.1	65.4	27.4(22.1)	31.9(26.2)
3	92.9	65.8	26.9(22.4)	30.1(25.3)
4	87.9	65.1	27.7(21.5)	25.3(20.3)
5	83.3	64.7	28.1(22.4)	20.7(14.6)
6	79.2	64.2	28.7(22.7)	16.1(10.4)
7	77.4	64.0	28.9(23.7)	14.9(10.2)
8	73.8	64.7	28.1(23.9)	10.1(5.8)
9	70.2	65.0	27.8(25.8)	5.8(4.4)
10	59.5	57.9	35.6(32.7)	1.8(neg. val.)
11	39.8	38.1	57.7(47.3)	1.9 " "
12	20.0	18.6	79.4(72.6)	1.6 " "
13	3.5	3.2	96.5(86.8)	0.0 " "

The first curve shows the saturated acid values found by the two methods. The second curve shows the linolic acid by the two methods, and the third curve the resi-



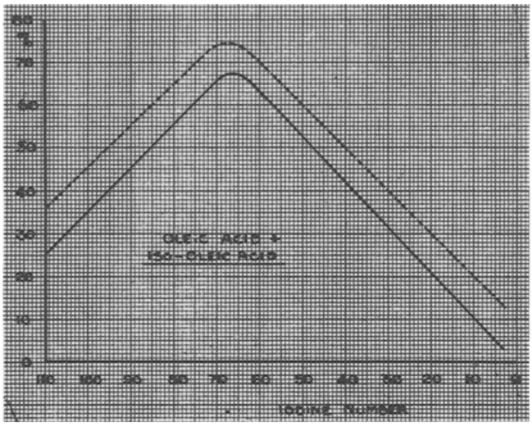
Curve I

dual oleic and iso-oleic acid. It was established before the investigation was started that iso-oleic acid behaves exactly like oleic acid with the Kaufmann reagent, and thus the presence and concentration of iso-oleic acid does not affect the determination.

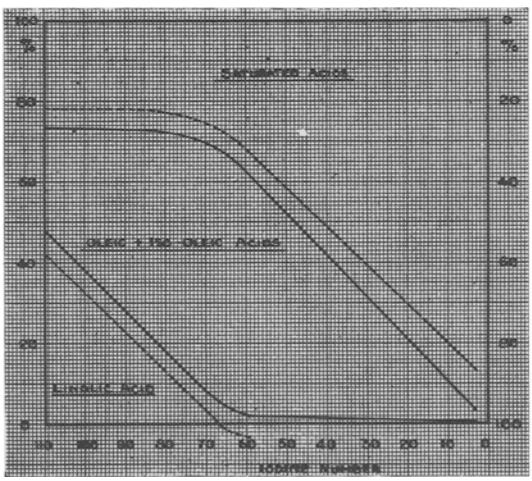


Curve II

The fourth curve shows a composite diagram from all these curves, showing the



composition of the product for each iodine number.



It is readily seen that a discrepancy of about 4% exists in both the linolic and saturated acid values by the two methods. However, the great convenience and rapidity of the Kaufmann value would recommend it as a plant control procedure, and if desired, the results may be made comparable with those from the Twitchell method by the subtraction of an appropriate correction. However, it is our opinion that the Kaufmann number determination probably gives the more nearly absolute results of the two methods. From table II it is readily seen that, in the last four samples at least, the saturated acid content found by the Twitchell method is too low for a product of the given iodine number, and if the linolic acid values are calculated from the Twitchell figures, impossible negative values are obtained. Thus in these samples at least, and probably in all the others, the Kaufmann value is the more absolute.

A further point to be noted in both the series is that there is practically no change in the Kaufmann number until the iodine number has been reduced to about 70 or 80, i.e. to the stage of a partially hydrogenated shortening. It follows from this fact that if the Kaufmann value of a batch of oil be determined once and for all, the linolic acid content of all the shortening batches made from this batch of oil can be calculated from the iodine value alone.

It is our opinion, therefore, that the Kaufmann value forms a very convenient index in the analysis of oils and fats, and gives values which are at least as accurate as those obtainable from the Twitchell method.

Niger Co., a subsidiary of Lever Bros., intends to exercise its option to repay the present outstanding £1,500,000 7% debenture stock issued in 1925. The stock is repayable on or after October 1, 1931 at 103% and the company proposes to repay the full amount on that date. Bulk of money needed for this procedure will be gotten by issue of 5% stock, carrying an unconditional guarantee of Lever Bros.

Turbo-Mixer Corp., New York, has leased additional space in the Crystal Building, 250 W. 43rd St., where the general offices, testing and research laboratories will now be consolidated. All manufacturing has been concentrated in one plant at Hudson, N. Y.

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