Iodine Values on Menhaden Fish Oil

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THE following experiments were undertaken in order to determine which of the existing methods is the quickest and most accurate for the determination of iodine values on Menhaden fish oil. Much work has been done along these lines since Hubl introduced his methods for the quantitative absorption of iodine of fats (J. S. C. I. 1884, 3,641) and even today his method is considered by many authorities as the most accurate. (Schmidt-Nielsen and Owe). It is claimed that the results obtained by the Hubl method are nearest to the theoretical values. One great disadvantage of the Hubl method however, is the long time required for the reaction, making it impossible for many industrial laboratories to use this method where rapid work is required.

Among the many other different methods there are only two of real practical value: The Wijs and the Hanus methods. All the other methods of test give more or less unreliable results as far as Menhaden Fish Oil is concerned. As stated before, much work has been done along these lines, but as far as we could find out after consulting a great deal of literature pertaining to iodine values, no comparative tests were ever made in order to find out how the values obtained by the two methods check up on the same material at different times given for the reaction.

The Wijs solutions used for the experiments was prepared as follows: 13 grams of resublimed iodine were dissolved in 1 liter of glacial acetic acid. When completely dissolved a blank was run with N/10 sodium thiosulphate solution and then dry chlorine was passed through the iodine solution until the first blank was exactly doubled. This solution was kept in an amber colored bottle. The Hanus Solution was made up by dissolving 13.5 grams of resublimed iodine in 1 liter of glacial acetic acid. When completely dissolved 3cc. of Bromine were added. This solution was also kept in an amber colored bottle. The iodine values were determined by weighing about 0.15 grams of oil into a wide-necked stoppered flask of 250 cc. capacity. The oil was dissolved in 15 cc. of chloroform and 25 cc. Wijs or Hanus solution added. After moistening the stopper of the flask with a 15 percent KI solution, the mixture was allowed to stand in the dark for the time required for the reaction. After standing, the stopper and neck of the flask were washed down with 15cc. of a 15 percent KI solution and the excess of iodine titrated with N/10 sodium thiosulphate solution, using 5 cc. conc. HCL and 20 cc. of a 1/N $K_2Cr_2O_7$ Two tests were run for each determination. In order to determine the strength of the sodium thiosulphate solution, 10 cc. of an exactly 10 percent KI solution were taken and 5 cc. conc. H1 and 20 cc. of a 1/N $K_2Cr_2O_7$ solution added. By this exactly 0.2 gram of iodine are liberated. This amount is titrated with the sodium thiosulphate solution to be tested and the strength calculated.

Great care was taken that all the flasks were absolutely clean and that all determinations were run at a temperature of 70°F.

The samples represented refined Menhaden fish oil:

#1 containing 2.75% free fatty acid
#2 " 4.08% " " "
#3 " 10.39% " " "

The results were as follows:

No. 1 Sample

Hanus		Wijs	
Time	Iodine Value	Time	Iodine Value
15 Min.	169.3	15 Min.	180.1
30 "	174.3	30 "	180.2
45 "	177.5	45 "	180.4
60 "	177.8	60 "	180.8
75 "	178.7	75 "	180.9
90 "	178.9	95 "	180.7
180 "	182.6	180 "	181.1

	No. 2 Sample		
15 Min.	170.0	15 Min.	179.4
30 "	170.2	30 "	180.0
45 "	175.0	45 "	180.2
60 "	175.0	60 "	180.4
75 "	178.7	75 "	180.3
90 "	179.8	90 "	180.5
180 "	182.3	180 "	181.7
	No. 3 Sample		
15 Min.	169.6	15 Min.	175.1
30 "	170.3	30 "	175.3
45 "	171.4	45 "	176.0
60 "	173.5	60 "	176.1
75 "	173.3	75 "	177.6
90 "	173.2	90 "	180.0
180 "	173.1	180 "	180.3

These figures show that the Wijs method requires less time for the reaction than the Hanus method. The iodine values by both methods increase relatively to the time allowed for the iodine absorption. However, the Wijs values show a very uniform increase; the values obtained by the Hanus method do not increase in the same proportions, but show a very irregular movement. The Wijs values increase very little after the first 15 minutes, whereas the Hanus values show a very great difference even between 90 and 180 minutes time allowed for the reaction. These facts prove that the reaction with the Wijs solution is almost completed after the first 15 minutes; the reaction with the Hanus solution is not completed even after 90 minutes. The Wijs values on sample #3 do not show the same uniform increase as on samples #1 and #2. It is possible that the high content of free fatty acids tends to retard the reaction. But even on this sample we can see that the figures show a far more uniform increase than the Hanus values, where even after 180 minutes the absorption does not seem to be completed.

From the above given facts we must come to the conclusion that the Wijs method is far more reliable and faster than the Hanus method for the determination of iodine values on fish oils. Furthermore, it is safe to say that the Wijs method requires not more than half an hour for oils up to 5 percent and one hour for oils containing over 5 percent free fatty acids as time required for the reaction. It is claimed that any excess of Chlorine (Schmids-Nielsen and Owe J. S. C. I. 1924, 43, B 302) in the Wijs solution tends to give unreliable results (too high), whereas Ueno (J. S. C. I. 1916, 35, 367) is not of the same opinion. After much experimenting along these lines, we must agree with Ueno. A Wijs solution containing a little excess of chlorine gives iodine values practically identical with those obtained with a so-called "normal" solution. A very large excess of chlorine in the solution gives too high values which however tend to become normal after the solution has been kept for several days. It is therefore advisable to let the solution stand for 2 or 3 days before using it. This procedure is much better than trying to adjust the solution with an iodine solution containing no chlorine.

A slight excess of iodine is of no advantage as far as we could see by running Iodine values with Wijs solution containing a slight excess of Iodine. The results were practically the same as those obtained by a solution containing an excess of Chlorine. However, it seems that a solution containing an excess of Iodine is not as stable as with an excess of Chlorine. In addition we made several experiments in order to find out if and to what degree the iodine values are effected by running the tests at different temperatures. These experiments revealed that for each 10°F over 70°F the value is increased by about 0.6, using either the Wijs or Hanus method.

2 samples representing refined Menhaden fish oil.

1. Sample—Wijs Method

At 70°F.	176.7
" 80°F.	177.3
" 90°F.	177.8
" 100°F.	178.5

2. Sample—Hanus Method

At 70°F.	175.0
" 80°F.	175.9
" 90°F.	176.5
" 100°F.	177.1

A newly patented oil-refining process provides for the admixture with the oil to be refined of dry powdered alkali intimately mixed with a finely divided solid adsorbent carrier material such as fuller's earth; and the addition of just sufficient water to promote rapid neutralization and agglomeration of the resultant soapstock. U. S. Pat. No. 1,705,825.