Calculating the Iodine Value for Marine Oils from Fatty Acid Profiles

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ABSTRACT: The iodine values of marine oils were directly calculated from fatty acid profiles by using reacting ratios (calculation factors) between I_2 (iodine) and either the fatty acids bound to a triglyceride or the free fatty acids. A total of 20 factors were incorporated from C14:1 to C24:1, placed into an Excel® spreadsheet, and used to calculate the iodine values. The calculated values were then compared to the oil's iodine value obtained by the traditional titration method. The results indicate that this method can be used to obtain the iodine value of marine oils directly from the oil's fatty acid composition, thus giving two results from one analysis.

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KEY WORDS: Fatty acid profile, free fatty acids, iodine value, marine oils, triglycerides.

The definition of the iodine value is the measurement of the unsaturation of fats and oils, and is expressed in terms of the grams iodine absorbed/100 g fat under standard conditions. The theoretical (or calculated) iodine value for a marine oil can be obtained by multiplying the percentage of each fatty acid contained in the marine oil with the reacting ratio of I_2 to either the free fatty acid, or the fatty acids bound to a triglyceride (hereafter designated triglyceride). The factors for 20 ratios, from C14:1 to C24:1, were calculated and used to obtain the theoretical iodine value of marine oils from their fatty acid compositions (1). The marine oils were also titrated (2) to determine their iodine value. A comparison of the results was performed with the triglyceride factors and can be found in Table 1. The comparison indicates that this method can be used to obtain the iodine value of marine oils directly from fatty acid compositions, and should be considered for use as a "Recommended Practice" to calculate iodine values. The factors for triglycerides and free fatty acids can be found in Table 2. There is a current AOCS Recommended Practice (3) to calculate the iodine value for edible oils directly from fatty acid compositions, but it lists only six acids and factors. This is adequate for edible oils but does not cover the large range of fatty acids that are found in marine oils. Because of the large number of factors (20) used to calculate the iodine values presented in Table 1, Excel spreadsheets were assembled in which the iodine value was automatically calculated when the fatty acid profile percentages were entered into the spreadsheet.

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EXPERIMENTAL PROCEDURES

The marine oil used in this study was menhaden fish oil. The titrated iodine values were obtained by AOCS Official Method Cd 1-25, "Iodine Value of Fats and Oils Wijs Method."

Methyl ester preparation. The methyl esters were prepared by AOCS Official Method Ce 2-66, "Preparation of Methyl Esters of Long-Chain Fatty Acids."

Gas-liquid chromatograph (GLC) system. The fatty acid profiles were obtained in an HP 5890 series GLC (Hewlett-Packard, Palo Alto, CA), coupled to an HP 3396A Integrator. A 30-m Supelcowax 10 column (0.53 mm i.d. and 1 µm film thickness, Supelco, Inc., Supelco Park, Bellefonte, PA) was used. The instrument settings were: injection temperature, 260°C; flame ionization detector temperature, 272°C; initial oven temperature held at 140°C for 1.73 min before ramping at 4.2°C/min to 181°C. The temperature was held for 2 min at 181°C before ramping at 1.8°C/min to 194°C, then ramping at 3.1°C/min to 233°C and held for 10.5 min. A split ratio of 9:1 was used with a column flow rate of 9.5 mL helium/min. A typical injection volume was 0.3 µL.

RESULTS AND DISCUSSION

Table 1 shows the results of a comparative study between the theoretical or calculated iodine value and the iodine value obtained by titration. The t-test (4) was applied to the data to determine whether a significant difference existed between the two methods. The variance of the differences $\{s_d \pm \text{sqrt}[\text{sum}(d - d_{avg})^2/N - 1]\}$ was determined to be 1.33. The t-value $[d_{avg}/s_d \times \text{sqrt}(N - 1)]$ was determined to be 2.94. The percentile value for Student t distributions (5) at 95% probability is $t_{0.975} = 2.57$, and at 99% probability it is $t_{0.995} = 4.03$. The results of the comparison would suggest that the difference between the two methods is significant, but the agreement between the two methods is satisfactory for marine oils, thus offering an alternative means of obtaining iodine values for marine oils when fatty acid compositions are being determined. This comparison also suggests that the method for calculating iodine values for marine oils from fatty acid profiles could be considered for use as a "Recommended Practice" for calculating iodine values.

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TABLE 1
Theoretical (calculated) vs. Titrated Iodine Values for Marine Oil Samples

Sample #	Calculated result	Titration result	Difference[a]	Difference[b] (%)	$(d - d_{avg})^{2\ c}$
1	178.2	176.5	1.7	0.95	0.0025
2	178.5	181.0	2.5	1.40	0.5625
3	162.8	159.8	3.0	1.84	1.5625
4	174.9	174.8	0.1	0.06	2.7225
5	174.2	174.4	0.2	0.11	2.4025
6	167.9	164.9	3.0	1.79	1.5625

[a]Average difference = 1.75.
[b]Average % difference = 1.03.
[c]Sum of $(d - d_{avg})^2$ = 8.815.

TABLE 2
Triglyceride and Free Fatty Acid Factors for Calculating Iodine Values

Fatty acid	Carbon and double bond number	Iodine number of triglyceride	Triglyceride factors	Iodine number of acid	Acid factors
Tetradecenoic (myristoleic)	14:1	106.17	1.0617	112.12	1.1212
Hexadecenoic (palmitoleic)	16:1	95.02	0.9502	99.76	0.9976
Hexadecadienoic	16:2	191.49	1.9149	201.11	2.0111
Hexadecatrienoic	16:3	289.44	2.8944	304.10	3.0410
Hexadecatetraenoic	16:4	388.89	3.8889	408.75	4.0875
Octadecenoic (oleic)	18:1	85.99	0.8599	89.85	0.8985
Octadecadienoic (linoleic)	18:2	173.16	1.7316	180.99	1.8099
Octadecatrienoic (linolenic)	18:3	261.54	2.6154	273.46	2.7346
Octadecatetraenoic	18:4	351.16	3.5116	367.27	3.6727
Eicosenoic (gadoleic)	20:1	78.53	0.7853	81.73	0.8173
Eicosadienoic	20:2	158.04	1.5804	164.54	1.6454
Eicosatrienoic	20:3	238.55	2.3855	248.43	2.4843
Eicosatetraenoic (arachidonic)	20:4	320.09	3.2009	333.43	3.3343
Eicosapentaenoic	20:5	402.68	4.0268	419.56	4.1956
Henicosapentaenoic	21:5	385.52	3.8552	400.97	4.0097
Docosenoic (erucic)	22:1	72.25	0.7225	74.96	0.7496
Docosatetraenoic	22:4	294.08	2.9408	305.30	3.0530
Docosapentaenoic	22:5	369.76	3.6976	383.95	3.8395
Docosahexaenoic	22:6	446.34	4.4634	463.57	4.6357
Tetracosenoic (selacholeic)	24:1	66.91	0.6691	69.23	0.6923

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