Clarification and Expansion of Formulas in AOCS Recommended Practice Cd 1c-85 for the Calculation of Iodine Value from FA Composition

Sir:

The iodine value (IV), or the number of grams of iodine that add to 100 g of fat, is a long-accepted measure of the unsaturation of edible oils (1,2). In spite of modern methods for the detailed determination of the FA composition of edible oils, the IV is still a widely recognized and useful parameter. In the last decades there has been great interest in the health benefits of consuming polyunsaturated fat, particularly fish oils, and the percent polyunsaturation is therefore of consumer interest. This percentage can be determined by GC, but an empirical formula to work this out from the IV has been published by Ackman (3), where % PUFA = 10.7 + 0.337 × (IV − 100). We can also work out the IV from the FA composition. Formulas to do this for a limited number of FA have been published in an AOCS recognized method (4). The method gives two formulas as shown below:

Triglycerides: IV = (% hexadecenoic acid × 0.950)
+ (% octadecenoic acid × 0.860) + (% octadecadienoic acid × 1.732)
+ (% octadecatrienoic acid × 2.616) + (% eicosenoic acid × 0.785)
+ (% docosenoic acid × 0.723) [1]

FFA: IV = (% hexadecenoic acid × 0.9976)
+ (% octadecenoic acid × 0.8986) + (% octadecadienoic acid × 1.810)
+ (% octadecatrienoic acid × 2.735) + (% eicosenoic acid × 0.8175)
+ (% docosenoic acid × 0.7497) [2]

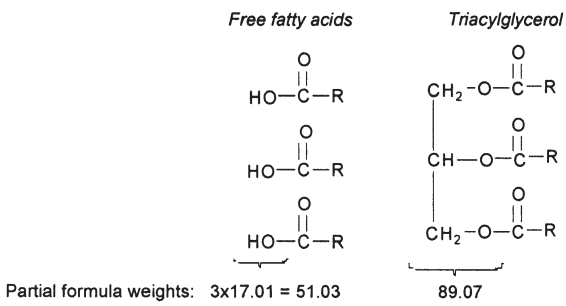
Since the rationale behind these two formulas and their applicability are not fully explained in the method, I feel that a more detailed discussion is in order. The two formulas will also be expanded to include other common unsaturated FA.

There is more than one way to express the FA composition of fat. The generally accepted way to do this in food nutrition tables is as grams of each acid per 100 grams of fat. This is the percent content of a particular FA in the fat. Percent FA composition, however, often refers to the relative amount of the FA in a mixture of the isolated FA or their methyl esters. This kind of information is obtained, for example, by capillary GC by integrating the peaks and determining the percentage of each FA peak of the total (5).

Summation of the FA content of all the FA in a particular fat as given in nutrition tables will not add up to 100, even if the fat is a pure TAG, because of the glycerol part of the fat. Summation of the FA composition figures as determined by peak integration will, however, give 100% (assuming all the FA are included) within experimental error. If we take pure tristearin ($C_{57}H_{110}O_6$, M.W. 891.51 g/mol) as an example, we see that the FA moieties are 90.01% of the fat. If expressed as FFA, this goes up to 95.73% of the total weight of the fat. The glycerol moiety is 9.99% of this fat, and 10.33% if expressed as free glycerol.

It is convenient to look first at Equation 2 for the FFA IV. The definition of IV is *g iodine per 100 g fat*. For any material, whether a mixture of FFA or any kind of fat, where the FA content is given as *g per 100 g* (the same as percentage of the total), a division of the fatty acid molecular weight (FA MW) into the percentage will give moles of that particular FA in 100 g of the material. For a monounsaturated FA, the number of moles of double bonds is the same, which reacts with the same number of iodine molecules. We can change this into grams of iodine by multiplying by its M.W., 253.80 g/mol. The factor for converting the percentage into IV is therefore 253.80/(FA MW). For example, for hexadecenoic acid (16:1, M.W. 254.41 g/mol) we have 253.80/254.41 = 0.9976; for 18:1 the factor is 253.80/282.47 = 0.8985; for 20:1 the factor is 253.80/310.52 = 0.8173; for 22:1 the factor is 253.80/338.57 = 0.7496. If we have more than one double bond in the FA, we simply multiply by the relevant number. Thus, the factor for 18:2 is (253.80/280.45) × 2 = 1.810 and for 18:3, (253.80/278.44) × 3 = 2.735. We can now add factors for FA that are not covered in the AOCS Cd 1 c-85 method. This is summarized for 13 unsaturated FA in Table 1.

Clearly, AOCS Cd 1 c-85 Equation 1, for the TG IV, is based on GC composition values, as will be shown. The raw figures obtained from the GC integrator give the relative amounts of the FA. If we take these to refer to FFA, we can also get a factor to convert the percentage figures into IV, but only if we have a pure TAG. The factor is worked out by taking into account the larger weight of the TAG, that is, three FA attached to glycerol, rather than the same three FA themselves. As illustrated in Scheme 1, the difference is equal to 89.07 – 51.03 = 38.04, or 12.68 g/mol FA. Thus, the factor for the relative FA composition is obtained by dividing the



SCHEME 1

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TABLE 1
Factors for Determining the Iodine Values (IV) of Fats from the Percent FA Content in the Fat[a]

FA	FA MW (g/mol)	No. of C=C	Factor	Factors in AOCS Cd 1 c-85, Equation 2
10:1	170.25	1	1.4907	
14:1	226.36	1	1.1212	
16:1	254.41	1	0.9976	0.9976
18:1	282.47	1	0.8985	0.8986
18:2	280.45	2	1.8099	1.810
18:3	278.44	3	2.7345	2.735
18:4	276.42	4	3.6727	
20:1	310.52	1	0.8173	0.8175
20:4	304.47	4	3.3343	
20:5	302.46	5	4.1956	
22:1	338.57	1	0.7496	0.7497
22:5	330.51	5	3.8395	
22:6	328.49	6	4.6358	

[a]Abbreviations used are as follows: 10:1 = decenoic acid; 14:1 = tetradecenoic acid; 16:1 = hexadecenoic acid; 18:1 = octadecenoic acid; 18:2 = octadecadienoic acid; 18:3 = octadecatrienoic acid; 18:4 = octadecatetraenoic acid; 20:1 = eicosenoic acid; 20:4 = eicosatetraenoic acid; 20:5 = eicosapentaenoic acid; 22:1 = docosenoic acid; 22:5 = docosapentaenoic acid; 22:6 = docosahexaenoic acid; FA MW, fatty acid molecular weight.

M.W. of iodine by the "fat" M.W. of each FA, that is, FA MW + 12.68, and multiplying by the number of double bonds. The factor for hexadecenoic acid is, for example, 253.80/(254.41 + 12.68) = 0.9502. The factors for the other common unsaturated FA are given in Table 2.

To illustrate the use of these formulas, let us take an example from a well-known lipid handbook (6). This book gives the "weight %" composition of olive oil. If that were true, we should use the factors for Equation 2 to work out the IV. However, these weight percentages, as do many others in the same handbook, add up to 100%, which must mean that we are not talking about FA percentages of the fat (g FA per 100 g of fat). If the figures refer to relative amounts of the FA, we should use the factors belonging to Equation 1. This is shown in Table 3, which illustrates a spreadsheet arrangement to work this out, with the spreadsheet formulas in column 5. The difference here is not great, but it becomes more significant with increasing unsaturation.

TABLE 2
Factors for the Determination of IV from the Relative FA Composition for a Pure TAG[a]

FA	FA MW + 12.68 (g/mol)	No. of C=C	Factor	Factors in AOCS Cd 1 c-85, Equation 1
10:1	182.93	1	1.3874	
14:1	239.06	1	1.0617	
16:1	267.11	1	0.9502	0.950
18:1	295.17	1	0.8598	0.860
18:2	293.15	2	1.7315	1.732
18:3	291.14	3	2.6152	2.616
18:4	289.12	4	3.5113	
20:1	323.22	1	0.7852	0.785
20:4	317.17	4	3.2008	
20:5	315.16	5	4.0265	
22:1	351.27	1	0.7225	0.723
22:5	343.21	5	3.6974	
22:6	341.19	6	4.4632	

[a]For abbreviations, see Table 1.

TABLE 3
Iodine Value (IV) of Olive Oil (Ref. 6), Worked Out According to Equations 1 and 2[a]

	A	B	C	D	E	F
4	FA	Weight %	Factor (Eq. 1)	Calculated IV	Factor (Eq. 2)	Calculated IV
5				=B5 × C5		=B5 × E5
6	16:0	10.3		0.00		0.00
7	16:1	0.7	0.9502	0.67	0.9976	0.70
8	18:0	2.3		0.00		0.00
9	18:1	78.1	0.8598	67.15	0.8985	70.17
10	18:2	7.3	1.7315	12.64	1.8099	13.21
11	18:3	0.6	2.6152	1.57	2.7345	1.64
12	20:0	0.4		0.00		0.00
13	20:1	0.3	0.7852	0.24	0.8173	0.25
14	Σ	100		82		86

The notes following the AOCS Recommended Practice Cd 1 c-85 state that the calculations tend to be low for low IV, and there are reservations for partially esterified material. I consider it more helpful to point out that, if the FA composition is expressed as percent FA of the total material, which can be done from GC data, the factors given in Table 1 will give the correct IV. It is also important to point out that the factors given for relative "raw" GC integrations are only strictly applicable for pure TAG. It seems to me that it would be very helpful if editors insisted that all FA composition data be reported as a percentage of the total material analyzed. Industry and traders would no doubt also welcome less ambiguity in the reporting of FA compositions of fat.

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5. See, for example, Sigurgísladóttir, S., and H. Pálmádottir, Fatty Acid Composition of Thirty-Five Icelandic Fish Species, *J. Am. Oil Chem. Soc. 70*:1081–1087 (1993).
6. Gunstone, F.D., J.L. Harwood, and F.B. Padley (eds.), *The Lipid Handbook*, Chapman & Hall, England, 1986, Table 3.71, p. 74.

Sigthór Pétursson*
Faculty of Natural Resource Sciences
University of Akureyri
600 Akureyri, Iceland

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*E-mail: sigthor@unak.is