Computer Determination of Chemical and Physical Values of Fats and Oils from GLC Fatty Acid Composition, Acid Value, and Titer

V. KOMAN, and J. KOTUC, Department of Microbiology and Biochemistry
Slovak Polytechnic University, 880 37 Bratislava, Janska 1, Czechoslovakia,
and Department of Computing Technic, Slovak Polvtechnic University,
801 00 Bratislava, Radlinsky 12, Czechoslovakia

ABSTRACT

A possibility for determination of 40 theoretically and industrially significant and frequently used values of triglyceride fats and oils with a digital computer is presented. An adequate computer program in the operational FORTRAN language was worked out for this purpose.The only input data are the experimental fatty acid compositions easily and quickly determinable by gas liquid chromatography, titrimetrically determinable acid value, and the titer.

INTRODUCTION

The advantages of gas liquid chromatographic (GLC) analysis, its rapidity, qualitative distinguishing ability, as well as its quantitative exactness for minute samples are well known. The use of computers makes it possible to manipulate large numbers of numerical and experimental results. If a combination of these two methods is possible, optimal relations between the number of data and their exactness are obtained in very short time. A method for the determination of a basic chemical constant of triglyceridic fats and oils—the iodine value—using GLC analysis of fatty acids and a constructed combined chart was described by Koman and Danielova (1). They also presented the possibility of determining eight important physico-chemical constants of fats and oils based on a single GLC analysis of fatty acids and using a constructed alignment chart (2). The principles and review of using digital computers and numerical methods for some problems of triglyceride fats and oils were discussed at a recent symposium (3).

The aim of the present paper is to elaborate on the possibility of constructing a computer program which, on the basis of only one GLC analysis of fatty acid mixture and from the determined acid value and also from the titer allows determination of the most frequently required physico-chemical constants. Further theoretically and technologically important information of triglyceride fats and oils is also obtained.

EXPERIMENTAL PROCEDURES

Materials and Methods

Plant oil samples extracted from the following industrially stored oilseeds were used: coconut, groundnut, sunflower, linseed, and rapeseed. Their acid values were 4.79, 10.1, 3.81, and 10.77 mg KOH/g, respectively. As an animal fat, a sample of commercial lard having an acid value of 0.33 mg KOH/g was used. Methyl esters prepared by direct inter esterification (4) were injected into the gas chromatograph.

Determination of iodine value was done according to Hanush using a solution of iodo monobromide and by back titration with 0.1 N solution of sodium thiosulphide (5). Determination of the saponification value was done by current method of the saponification of the sample with 0.5 N alcohol solution of KOH followed by titration with 0.5 N alcohol solution of hydrochloric acid (5). The acid value was determined by simple titration of fatty oil samples with 0.1 N KOH in ethanol (5).

The freezing point of free fatty acids—titer—was determined after saponification in Zhukow's device (5).

The algorithm sequences for computer determination of the values and data for triglyceride samples were translated into the programming FORTRAN IV language.

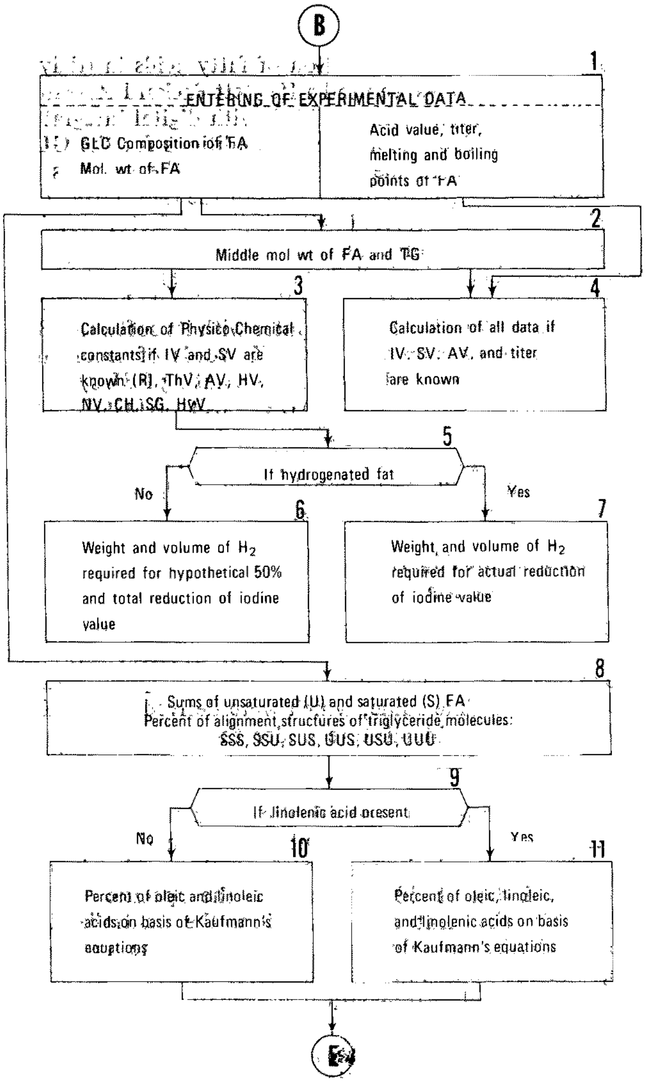

FIG. 1. Simplified form of the flow chart of algorithm for computer determination of triglyceride fats and oils values and data. AV = acid value, CH = heat of combustion, FA = fatty acids, HV = hydroxyl value, HyV = hydrogen value, IV = iodine value, NV = neutralization value, RI = refractive index, SG = specific gravity, SV = saponification value, TG = triglycerides, and ThV = thiocyanogen value.

TABLE I

Fatty Acid Compositions of Triglyceridic Fatty Oil Samples as Found by GLC Analysis and Experimentally Determined Acid Values and Titers

Fatty acids		Coconut oil	Peanut oil	Sunflower oil	Linseed oil	Rapeseed oil	Lard
		Fatty acids (%)					
Caprylic	($C_{8:0}$)	7.48	—	—	—	—	—
Capric	($C_{10:0}$)	6.23	—	—	—	—	0.18
Lauric	($C_{12:0}$)	50.31	0.15	—	—	—	0.11
Myristic	($C_{14:0}$)	20.07	—	—	—	—	1.52
Palmitic	($C_{16:0}$)	8.51	17.40	7.06	8.77	3.84	23.73
Palmitoleic	($C_{16:1}$)	—	0.60	—	—	0.32	3.35
Stearic	($C_{18:0}$)	2.76	2.30	9.41	5.67	1.49	15.16
Oleic	($C_{18:1}$)	4.64	39.00	23.33	21.98	14.77	45.42
Linoleic	($C_{18:2}$)	—	37.00	56.66	12.26	15.12	8.81
Linolenic	($C_{18:3}$)	—	1.38	2.10	51.32	6.29	0.51
Eicosenoic	($C_{20:1}$)	—	2.62	—	—	9.44	0.74
Erucic	($C_{22:1}$)	—	0.55	—	—	47.93	—
Acid value		4.94	10.10	3.81	0.11	10.77	0.33
Titer		23.40	29.70	18.90	17.70	11.20	37.00

Equipment

To determine the composition of fatty acids in triglyceridic fatty oil samples we used a Hewlett-Packard Research Gas Chromatogrraph model 7620 A with digital integrator model 3370 A. The experimental conditions for the GLC analysis of fatty acid methyl esters were the same as in Reference 1. The quantitative results of the GLC fatty acid analysis were not corrected with response factor nor by internal or external standards.

For determination of all important values and data of the triglyceride samples by using the constructed program, we first used a Minsk 22 M computer with its software: 8K words of primary memory, 1600 K words of secondary memory, operation speed 6000/sec, operating FEL system, and programming languages SADR, MAT, ALGOL, and FORTRAN. Later the computer program was rearranged for Siemens computer model 4004/150 with its 512 K byts of primary memory, operational speed 300,000/sec, and with all its software and hardware.

Conditions for the Algorithm and Program Construction

The algorithm of the computer program for determination of the most important vluaes of triglyceride fats and oils evolves from such basic constants as the saponification value and the iodine value, which were derived from GLC analysis of fatty acid mixture under the same conditions and mathematic formulations as described in our previous publications (1,2).

After the iodine and saponification values are obtained, conditions are fulfilled for computer determination of additional physico-chemical constants from them. That is, the refractivity index at 40 C and 60 C, the specific gravity (15 C/15 C), the heat of combustion, the neutralization value, the hydrogen value, the acetyl value, the hydroxyl value, and iodine saponification factor are computed by employing general mathematical formulations as listed in Reference 2.

Computation of further values is possible if in addition to the iodine and saponification values, the acid value and titer are known. There are ca. 15 possible values under these conditions. For these calculations are employed mathematical formulations which were found in References 6 and 7.

Computation of the weight and volume amounts of hydrogen required for hypothetical and/or actual reductions of the iodine values in unhydrogenated and hydrogenated triglyceridic fatty oils are incorporated into the computing program using instructions for the conditional branching.

The calculation of alignment structures of triglyceridic molecules, i.e., SSS..... UUU (regardless of their exact position, determination of which is possible after application of pancreatic lipase only) involves a simple summation of saturated (S) and unsaturated (U) fatty acids after their input and after their substitutions into the Vander Wal's expressions (8).

Also, the calculation of the melting points of fats and oils is incorporated into the algorithm of the presented computer program; multiples of weight averages of fatty acids with their tabular melting point values are employed in these calculations.

At the end of the proposed computer program is added a control recalculation of the contents of oleic, linoleic, or linolenic acids using Kaufmann's equations with their empirical constants (9). For iodine and thiocyanogen values as well as the sums of saturated fatty acids substituted in these equations, the ones obtained in previous calculation steps were employed. Presence or absence of linolenic acid is in this case a conditional branching instruction.

The qualitative parameters of individual fatty acids determined by GLC analysis were coded for input and output by two groups of numbers separated by a colon. The number before the colon indicates the number of carbon atoms in the molecule of a fatty acids, and the number after the colon represents the number of double bonds.

RESULTS AND DISCUSSION

In earlier papers (1,2) on the basis of only one GLC analysis of fatty acids and their constructed combined or alignment charts, it was possible to determine eight basic physico-chemical constants of triglyceride fat and oil samples. In this paper, GLC determined fatty acid compositions are processed in such a way that at the output of the computer 40 theoretically and industrially important values and data may be read. A simplified form of flow chart of the algorithm of such a computer program is interpreted with sequences in Figure 1.

Using GLC, the experimentally determined fatty acid composition in triglyceride samples as well as experimentally determined acid values and titers are listed in Table I. These are practically all the input data required by the instructions, statements, and commands of the constructed computer program in operational FORTRAN

TABLE II

Output Data of Fatty Oil Samples Obtained Using Data from Table I and Computer Program

Numeration	Values and data	Coconut oil	Peanut oil	Sunflower oil	Linseed oil	Rapeseed oil	Lard
1	Average of mol wts of fatty acids	210.91	280.74	269.82	277.96	308.11	273.21
2	Average of mol wts of triglycerides	670.73	880.23	847.46	871.89	962.33	857.64
3	Saponification value	250.96	191.23	198.62	193.06	174.91	196.26
4	Saponification equivalent	223.58	293.41	282.49	290.63	320.78	285.88
5	Iodine value of fatty acids	4.17	108.96	129.29	182.32	101.83	62.11
6	Iodine value of triglycerides	3.94	102.97	122.18	182.29	96.22	58.70
7	Hydrogen value	0.03	0.82	0.97	1.37	0.76	0.47
8	Thiocyanogen value	4.17	74.27	80.37	131.90	76.25	50.41
9	Iodine saponification factor	247.02	88.26	76.45	20.76	78.69	137.57
10	Hardness number	333.60	198.15	146.38	86.25	120.13	274.47
11	Neutralization value	265.82	199.86	207.93	201.85	182.13	205.35
12	Ester value	236.02	181.13	194.81	192.95	164.14	195.93
13	Hydroxyl value	4.66	9.66	3.64	0.11	10.34	0.32
14	Acetyl value	4.65	9.59	3.63	0.11	10.26	0.32
15	Specific gravity (15 C/15 C)	0.92334	0.91928	0.92419	0.92954	0.91345	0.91460
16	Heat of combustion	9079.81	9527.31	9440.43	9441.24	9683.33	9525.49
17	Refractivity index (40 C)	1.45196	1.46356	1.46581	1.27168	1.46277	1.45837
18	Refractivity index (60 C)	1.44721	1.45818	1.46047	1.46671	1.45739	1.45310
19	Percent of triglycerides	98.25	95.16	98.25	99.95	94.32	99.85
20	Percent of bonded fatty acids	92.65	90.85	93.77	95.59	90.36	95.42
21	Percent of fatty acids of neutral fat	94.31	95.46	95.44	95.64	95.80	95.57
22	Percent of free fatty acids	1.858	5.054	1.832	0.054	5.913	0.161
23	Splitting degree percent	1.968	5.282	1.918	0.057	6.157	0.168
24	Percent of glycerol	13.46	9.91	10.66	10.55	8.98	10.72
25	Specific heat of triglycerides (cal)	0.65	0.75	0.74	0.75	0.78	0.74
26	Specific heat of soap (cal)	0.32	0.34	0.34	0.34	0.35	0.34
27	Need of NaOH (35%) for saponification (g/1000 g)	512.67	390.65	405.76	394.39	357.32	400.94
28	Saponification heat of 1000 g of fat (kcal)	60.00	60.00	60.00	60.00	60.00	60.00
29	Amount of steam equal to the saponification heat (liters/min)	133.21	133.21	133.21	133.21	133.21	133.21
30	Weight equivalent of hydrogen by total reduction of iodine number (g/1000 gr)	0.31	8.13	9.65	13.61	7.60	4.64
31	Volume equivalent of hydrogen by total reduction of iodine number (ml/1000 g)	3940.65	102967.79	122175.29	172293.81	96224.83	58695.05
32	Weight equivalent of hydrogen by hypothetical 50% reduction of iodine value (g/1000 g)	0.16	4.09	4.85	6.84	3.82	2.33
33	Volume equivalent of hydrogen by hypothetical 50% reduction of iodine value (ml H_2/1000 g)	1970.33	51,483.89	61,087.64	86,146.91	48,112.42	29,347.53
34	Percent of saturated (S) fatty acids	95.36	19.85	14.47	14.44	5.33	40.70
35	Percent of unsaturated (U) fatty acids	4.64	81.15	82.09	85.56	93.87	58.83
36	Percent of simple molecular structures of triglyceride molecules:						
36a	SSS	86.716	0.782	0.303	0.301	0.015	6.742
36b	SUS	4.219	3.197	1.719	1.784	0.267	9.745
36c	SSU	8.439	6.395	3.438	3.568	0.533	19.490
36d	USU	0.205	13.072	9.751	10.571	4.697	14.086
36e	UUS	0.411	26.144	19.502	21.142	9.393	28.172
36f	UUU	0.010	53.440	55.319	62.632	82.714	20.361
37	Melting point of fatty acids (calc.) (C)	44.40	17.21	9.44	5.67	22.43	33.35
38	By Kaufmann's equations: Oleic acid percent	4.70	39.20	27.66	45.77	60.76	44.39
39	Linoleic acid percent	-0.03	41.42	58.28	-34.87	49.25	20.08
40	Linolenic acid percent		-0.47	-0.41	74.65	-15.34	-5.17

TABLE III

Classically and Computer Determined Iodine and Saponification Values

	Fatty oil samples					
Constant	Coconut oil	Peanut	Sunflower	Linseed	Rapeseed	Lard
Iodine value						
Classically determined	4.20	99.0	129.50	181.50	103.50	59.70
Computer determined	3.94	102.97	122.18	182.29	96.22	58.70
Saponification value						
Classically determined	265.30	191.00	183.90	186.60	170.60	188.00
Computer determined	250.96	191.23	198.62	193.06	174.91	196.26

language.

Listed in Table II are all alphanumerical data for triglyceride fat and oil samples used in these experiments. The data were obtained from GLC analysis under conditions described by the computer program represented in Figure 1.

Classically-titrimetrically determined iodine and saponification values are compared with computed values in Table III. It can be seen that the computed values are, in comparison with those determined titrimetrically, 4% lower on the average. The contrary is true in the case of saponification values. There, the computing values are, on the average, 3% higher. Such differences of iodine and saponification values can affect, in our case, all the other data, obtained by using these two basic chemical constants. However, taking into account the great number of results and the shorter time in obtaining them, the mentioned differences can be labeled as "tolerable." Moreover, a greater accuracy of results can be expected after correcting the quantitative GLC analysis of fatty acids with response factors and internal or external standardization methods.

It is necessary to mention that all the data for triglyceride fat and oil samples determined by computing programs are theoretical only. In the present case, their accuracy will be in direct ratio with input analysis of fatty acids or the basic constants of iodine and saponification values derived from it.

Other constants than those of iodine, saponification, and acid values or titer were not experimentally determined for the needs of the constructed computer program, and neither were they compared. Sufficient for the needs of the described computer program are the basic input data given in the first block of the flow chart in Figure 1. On the other hand, most of the data in Table II (approximately from item 20 and on) can only be obtained by computation.

The percentage values of alignment structures of triglyceridic molecules, i.e., SSS . . . . . UUU, included in the program, without pancreatic lipase application, are mostly of an information character. Despite that, such data can have some practical meaning. Trisaturated SSS structures of triglyceridic molecules determined as described should be in close relation with experimental results (10). The computing program for positionally exact determination of all, that is aligned and individual structures of triglyceridic molecules in their various concentration relations using qualitative–quantitative input data of fatty acids, defined after application of pancreatic lipase, forms the subject of a separate paper (Koman and Kotuc, unpublished data).

Some remarkable differences can be seen between the values of C_{18} unsaturated fatty acids determined experimentally by GLC analysis and those which were computed using the Kaufmann equations with the substituted values of the iodine value, thiocyanogen value, and sum of calculated saturated fatty acids. This computation was incorporated into the program because of its control possibilities. If we assume that GLC analysis is qualitatively as well as quantitatively one of the most precise methods for analysis of fatty acid mixtures, then the found differences of C_{18} unsaturated fatty acids can probably be explained by the fact that the original empirical constants in Kaufmann's equations are less exact and, for some theoretical aspects, can be corrected by the presented procedure.

The program for computer determination of important values of triglyceride fats and oils given in this paper is as general as possible. Among its advantages are a minimum of required experimental input data, adaptability to the exactness of input GLC analysis of fatty acids, completeness of results, lucid interpretation of input and output data and easy orientation in them, and finally a direct tabular format of the obtained results. The whole run times by using Minsk 22 M and Siemens 4004/150 computers were 18.2 min and 181 sec, respectively.

ACKNOWLEDGMENTS

We are thankful to Dr. K. Smidzarova for help in programming, to Dr. A. Lackova and Mrs. M. Bystricka for intensive technical assistance, and to Prof. St. Bachraty for his advice.

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[Received August 11, 1975]