# How Good are Analyses of Oils by GLC?[1]

S. F. HERB and V. G. MARTIN,
Eastern Utilization Research and Development Division, ARS, USDA, Philadelphia, Pa. 19118

## Abstract

Analyses of the fatty acid composition of 2 methyl ester mixtures and 13 oils, obtained by collaborators from the AOCS Smalley Gas Chromatography Check Program, were treated statistically. The statistical data may be interpreted to indicate groups of analysts who made a good, satisfactory or poor analysis. The data also indicate the relative degree of difficulty of analyzing the various oils. Coconut oil was the most difficult to analyze while safflower oil offered the least difficulty. A comparison of the precision of results employing the thermal conductivity detector and the flame ionization detector shows no difference.

## Introduction

Gas liquid chromatography (GLC) is universally accepted as the fastest and most reliable way to determine the fatty acid composition of fats and oils. Today, after a decade of common usage, we are continually asking "how good or how accurate are these analyses?"

The Smalley Gas Chromatography Subcommittee of the American Oil Chemists' Society is composed of a group of analysts from industrial, independent, university and government laboratories from the United States, Canada and Sweden. It has as its objective the promotion of better and more uniform analyses. Organized four years ago, it was first faced with the task of estimating the true composition of an oil and grading the analysts. This was accomplished in the following manner: a median was chosen by arranging the reported percentage of each component from the least value to the greatest value. The median is the percentage found in the position determined from the formula $(n + 1)/2$, where n is the number of values reported. It was found that the median usually gave a better value than the arithmetic mean, because it is not affected by extremes. Later we will demonstrate that a trimmed mean is equally as good and is more amenable to statistical analysis. For each collaborator, the deviation from the median was determined for each component of the sample; the sum of the deviations of all components by a collaborator resulted in a total deviation which represented the number of percentage units that the collaborator differed from the median. The sum of the medians approximates 100% of the sample, so when the total deviation was subtracted from 100, we obtained a percentage which represented the accuracy of the collaborator in determining the median values. Only those components of the sample that were reported by at least one half of the collaborators were retained for calculation of a grade.

This procedure was reasonably satisfactory for grading purposes, but the results did not indicate how well one made an analysis except in relation to the other collaborators. It did not indicate the percentage of collaborators making a satisfactory analysis or, for that matter, indicate what is a satisfactory analysis.

The present paper will describe a procedure which will indicate the accuracy of analysis, how well a collaborator has analyzed the sample, and a measure of the relative degree of difficulty in analyzing an oil. The data would enable any analyst to compare his results with those of the Smalley group.

## Experimental Procedures

Analyses by GLC were made employing a wide variety of columns and conditions. The AOCS Smalley Gas Chromatography collaborators were permitted to use the procedure they found best in their laboratory. Table I shows the variety of instruments, liquid phases, supports, column dimensions and conditions reported by the collaborators in the 1968–1969 series. This data is similar to that reported previously (1). It has been shown that these differences will not affect the results, provided one uses a reference sample for standardization and employs good analytical techniques (1).

The mode of integration employed had little or no effect on the results of the analyses. If we consider the four best analyses of each of the 13 oils reported, we find that 25 collaborators used a disc integrator, 19 an electronic integrator, 5 employed triangulation, 2 used the equation peak height × retention time, and 1 collaborator employed a planimeter. These ratios are in the approximate proportion that these procedures were employed by all collaborators.

## Discussion

The data reported by the collaborators were examined to determine which fatty acids were deemed to be present. It was arbitrarily decided that data for all acids reported by at least 50% of the collaborators would be retained. Data were punched on cards and fed to an 1130 IBM computer, programmed to make the following calculations:

1. Normalize the results from all analysts, since analyses may not add to 100% as a result of discarding some reported acids.
2. Calculate a mean, deviation from the mean, and standard deviation for each acid. Discard all values exceeding two standard deviations and recalculate a new mean.
3. Normalize the trimmed means since they may not add up to 100% after discarding some values. [It was found that the means adjusted in this manner agreed exceptionally well with the known composition of standard mixtures (Tables II and IV).]
4. Calculate the collaborator's deviation from the trimmed means. (When known mixtures are analyzed, the deviations from the known values are calculated.)
5. Calculate the standard deviation around the trimmed mean for each acid. Only data from separated acids are used. If two acids are reported as one acid, as in the case of coincident peaks, these data are rejected for these determinations.
6. Add the standard deviations for each component of the oil to give a value similar to a standard deviation of the total sample. (Analysis of each acid is dependent on every other acid in the oil and, therefore, the errors are additive.) This value indicates the accuracy expected for an analysis and the degree of difficulty in analyzing the oil.

[1] Presented at the AOCS Meeting, Minneapolis, October 1969.

TABLE I

Operating Conditions Reported by Collaborators for Analysis of SGC 22 Cottonseed Oil AOCS Smalley Gas Chromatography Series, 1968–69

| Lab. | Instrument[a] | Liquid phase | Support | Length, ft. | Diam., in. | Temperature | | | Carrier gas | | Sample | | Detector[b] | Integration |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Column, C | Flash heater, C | Det., C | Type | Flow, ml/min. | Size | Dilution | | |
| 2C | Aero-2100 | 5% EGA-Stab. | 100/120 Celite, AW, Sil. | 5 | 5/32 | 170 | 220 | 220 | $N_2$ | 40 | 25 μg | 3% $CHCl_3$ | FI | Disc |
| 3C | Aero-1520 | 5% BDS | ..... | 8 | 3/32 | 188 | 270 | 215 | $N_2$ | 25 | 90 μg | 10% Hexane | FI | Disc. |
| 5C | Aero-90P3 | 15% DEGS | 60/70 Anakrom ABS | 5½ | 3/16 | 205 | 290 | 290 | He | 120 | 0.4 ml | No | TC | Elect. |
| 6C | MicroTek 200R | 10% DEGS | 60/80 Chrom W, HMDS | 4 | ¼ | 150–200 <5°/min> | 240 | 275 | He | 80 | 1.0 μl | 1:10 | FI | Elect. |
| 7C | P.E.-800 | 15% DEGS | 80/100 Chrom W, AW | 12 | ⅛ | 130 → prog. | 280 | 150 | He | 80 | 20 μg | 1:20 $CH_3OH$ | FI | Elect. |
| 8R | Aero-A90P3 | 20% DEGS | 60/80 Chrom W, AW | 12 | ¼ | 190 | 245 | 225 | He | 40 | 2 μl | Yes | TC | Disc |
| 9R | P.E.-800 | 15% DEGS | Anakrom ABS | 10 | ⅛ | 200 | 250 | 220 | $N_2$ | 40 | 0.03 mg | 1:30 | FI | Triang. |
| 10 | Aero-90A | 20% DEGS | 80/100 Chrom W, AW, DMCS | 10 | 5/32 | 174 | ..... | 204 | He | 50 | 0.4 μl | No | TC | Triang. |
| 11 | Aero-A90P | EG Phthalate | Chrom P | 8 | ..... | 208 | 255 | 263 | He | ..... | 1.0 μl | No | TC | Disc |
| 12C | F&M-700 | 20% DEGS | 60/80 Chrom W | 8 | 5/32 | 190 | 260 | 230 | He | 80 | 1.0 μl | 1:10 | FI | Disc |
| 13R | B.C.-5000 | 20% DEGS | 60/80 Chrom W, AW | 6 | 3/16 | 180 | 250 | 250 | $N_2$ | 40 | 0.5 μl | Yes | FI | Triang. |
| 14C | F&M-720 | 20% DEGS | ..... | 6 | 5/32 | 200 | 250 | 250 | He | 90 | 0.5 μl | No | TC | Elect. |
| 15R | B.C.-10 | 20% EGG[c] | 90/100 Anakrom AB | 8 | ⅛ | 190 | 300 | 210 | Ar | 25 | 0.15 μl | No | FI | Elect. |
| 16C | Aero-A100 | 20% EGG[c] | 90/100 Anakrom AB | 6½ | ⅛ | 192 | 260 | 192 | He | 32 | 0.5 μl | No | TC | Disc |
| 17 | Aero-1520 | 20% DEGS | 60/80 Chrom P, AW | 10 | ⅛ | 215 | 235 | 235 | He | 50 | 0.2 μl | No | FI | Disc |
| 19C | F&M-720 | 25% DEGS | Gas Chrom P | 6 | 3/16 | 190 | 300 | 300 | He | 75 | 5 μl | 1:3 benzene | TC | Elect. |
| 21C | Aero-A-90 | 12% DEGS | 60/70 Anakrom ABS | 6 | 3/16 | 180 | 295 | 310 | He | 80 | 2 μl | 150 mg/ml | FI | Disc |
| 22C | F&M-810 | 20% EGG[c] | Chrom W | 6½ | ⅛ | 196 | 280 | 196 | He | 78 | 1.0 μl | No | TC | Triang. |
| 23 | F&M-810 | 15% DEGS | 80/100 Chrom W, AW | 8 | 3/16 | 200 | 280 | 260 | He | 100 | 0.5 μl | 1:3 | FI | Elect. |
| 26C | F&M-810 | 10% DEGS | 60/80 Diatoport-S | 9 | 3/16 | 185 | 300 | 300 | He | 60 | 0.8 μl | 5% | FI | Disc |
| 27C | Aero-A90-P3 | 20% DEGS | 60/80 Chrom W, HMDS | 10 | 5/32 | 190 | 220 | 240 | He | 75 | 0.5 μl | Yes | TC | Disc |
| 28C | Aero-Hify III | 15% DEGS | 60/80 Chrom W, DMCS | 8 | ⅛ | 205 | 270 | 275 | $N_2$ | 26 | 2.0 μl | 1:80 | FI | Disc |
| 30 | J.A.-700 | 17% EGA-Stab. | ..... | 8 | 3/16 | 210 | 230 | 230 | $N_2$ | ..... | 0.7 μl | No | FI | Triang. |
| 31R | P.E.-900 | 15% EGSSX | 100/120 Gas Chrom Q | 6 | 5/32 | 170 | 230 | 215 | $N_2$ | 30 | 80 μg | 2% Hexane | FI | Elect. |
| 32 | Aero-Hify 600 | 15% DEGS | ..... | 10 | 7/32 | 190 | 250 | 250 | He | 30 | 0.01 μl | 1:10 | FI | Disc |
| 33C | F&M-700 | 12% DEGS | 60/80 Gas Chrom | 4 | ⅛ | 180 | 280 | 280 | He | 30 | 0.6 μl | 35% | FI | Disc |
| 35C | F&M-810 | 18% DEGS | 60/80 Chrom W, AW | 10 | 7/32 | 210 | 300 | 280 | He | 85 | 0.5 μl | 1:1 | TC | Comp. |
| 36C | Homemade | 25% EGS | 40/60 Chrom W, AW, BW | 8 | ⅛ | 195 | 215 | 196 | He | 56 | 0.3 μl | No | TC | Elect. |

[a] Aero = Varian Aerograph; P.E. = Perkin-Elmer; B.C. = Barber-Colman; F&M = Hewlett Packard; J.A. = Jarrell-Ash.
[b] FI, flame ionization; TC, thermal conductivity.
[c] $H_3PO_4$ added.

TABLE II

Normalized Fatty Acid Analysis; SGC 19 Me Ester Mixture AOCS Smalley Gas Chromatography Series, 1968–69

| Laboratory | 14:0, % | 16:0, % | 16:1, % | 18:0, % | 18:1, % |
|---|---|---|---|---|---|
| 2C[a] | 11.76 | 23.46 | 6.24 | 13.24 | 45.30 |
| 3C | 12.02 | 23.35 | 7.45 | 12.71 | 44.47 |
| 5C | 11.53 | 23.54 | 6.11 | 14.15 | 44.67 |
| 6R | 11.54 | 23.77 | 6.48 | 12.52 | 45.70 |
| 7C | 11.62 | 23.32 | 6.32 | 12.36 | 46.37 |
| 8R | —13.15 | —25.34 | 7.31 | 12.57 | —41.63 |
| 9R | 11.20 | 23.92 | 6.57 | 13.34 | 44.96 |
| 10 | 11.61 | 23.61 | 6.99 | 13.03 | 44.75 |
| 11 | 11.72 | 22.96 | 6.99 | 14.06 | 44.27 |
| 12C | 11.41 | 23.14 | 6.34 | 13.45 | 45.66 |
| 13C | 11.74 | 24.13 | 6.38 | 13.25 | 44.49 |
| 14C | 12.74 | 23.30 | 6.95 | 13.10 | 43.90 |
| 15 | 11.45 | 23.64 | 6.81 | 13.51 | 44.59 |
| 16C | 11.48 | 23.61 | 6.59 | 13.67 | 44.66 |
| 17R | 12.31 | 24.45 | 6.71 | 12.68 | 43.85 |
| 18 | 11.39 | 23.28 | 7.16 | 14.18 | 44.00 |
| 19C | 11.89 | 23.76 | 6.83 | 12.94 | 44.58 |
| 21C | 11.69 | 24.40 | 6.54 | 12.96 | 44.40 |
| 22C | —13.37 | 23.76 | —10.71 | 12.17 | —39.98 |
| 23 | 11.63 | 23.35 | 7.11 | 13.45 | 44.45 |
| 25C | 12.04 | 23.49 | 6.79 | 12.82 | 44.86 |
| 26C | 11.19 | 22.78 | 7.25 | 13.66 | 45.13 |
| 27 | 12.62 | 24.45 | 6.81 | 13.12 | 43.00 |
| 28 | 12.18 | 23.73 | 7.34 | 13.04 | 43.76 |
| 30C | 12.52 | 24.13 | 7.08 | 12.74 | 43.53 |
| 31R | 11.60 | 23.70 | 6.79 | 13.34 | 44.58 |
| 32C | 12.25 | 23.89 | 8.33 | 12.32 | 43.21 |
| 33C | 11.12 | 24.37 | 6.12 | 11.62 | 46.77 |
| 34 | —13.45 | —26.66 | 6.20 | —6.57 | 47.12 |
| 35C | 11.84 | 23.52 | 6.96 | 13.12 | 44.56 |
| 36 | 11.42 | 23.43 | 6.79 | 12.61 | 45.75 |
| Trimmed means | 11.76 | 23.66 | 6.81 | 13.05 | 44.72 |
| Known values | 11.80 | 23.60 | 6.90 | 13.10 | 44.60 |
| Difference | 0.04 | 0.06 | 0.09 | 0.05 | 0.12 |

[a] Abbreviations: C, corrections applied; R, no corrections but response of detector checked; and —, values rejected (to obtain trimmed mean).

7. Calculate the total deviation of each analyst by summing the deviation of each component of the sample.

8. Grade each analyst by subtracting the total deviation from 100. The value is equal to the collaborator's accuracy in determining the composition of the total sample.

Table II shows a part of the computed data. It presents the results of the analysis of a known mixture of methyl esters. Throughout this paper shorthand designation will be given to various fatty acids, i.e., 16:0, 18:0 and 18:1, where the number to the left of the colon indicates the number of carbons in the chain and the number to the right indicates the number of double bonds. The values are the average of duplicates and have been normalized to 100%. The mixture is a reference standard recommended by the AOCS for use when analyzing corn, cottonseed, soybean, safflower, sunflower, sesame, poppyseed, walnut, kapok and rice bran oils to obtain correction factors, if necessary, and is designated as SGC 19 in this study. Table II shows rejected values by applying the restriction that values should lie within two standard deviations. The known composition is compared with the trimmed, normalized means which are in amazingly good agreement. It should also be pointed out that the laboratory numbers are those assigned each year, and the same number does not designate the same laboratory throughout; further, gaps in numbers are not laboratories eliminated for some reason, but simply mean that the laboratory assigned to that number did not report an analysis.

Table III shows deviations from known values (in the case of oils, they would be from the mean). Minus signs indicate rejected deviations when calculating the standard deviation of each component. The calculation of the standard deviation of each component is made using the equations: standard deviation (known) = $\sqrt{\Sigma(d)^2/n}$ where d = deviation from

TABLE III

Deviations and Grades; SGC 19 Me Ester Mixture AOCS Smalley Gas Chromatography Series, 1968–69

| Laboratory | 14:0, % | 16:0, % | 16:1, % | 18:0, % | 18:1, % | Tot. Dev., % | Grade, % | Ordered grades, % |
|---|---|---|---|---|---|---|---|---|
| 2C[a] | 0.040 | 0.140 | 0.658 | 0.138 | 0.701 | 1.677 | 98.32 | 99.76 |
| 3C | 0.220 | 0.250 | 0.550 | 0.390 | 0.130 | 1.540 | 98.46 | 99.50 |
| 5C | 0.271 | 0.061 | 0.785 | 1.051 | 0.066 | 2.234 | 97.77 | 99.49 |
| 6R | 0.261 | 0.168 | 0.421 | 0.581 | 1.095 | 2.526 | 97.47 | 99.34 |
| 7C | 0.178 | 0.275 | 0.579 | 0.738 | 1.769 | 3.539 | 96.46 | 99.09 |
| 8R | −1.350 | −1.740 | 0.410 | 0.530 | −2.970 | 7.000 | 93.00 | 99.00 |
| 9R | 0.599 | 0.322 | 0.329 | 0.241 | 0.364 | 1.856 | 98.14 | 98.88 |
| 10 | 0.189 | 0.012 | 0.091 | 0.069 | 0.154 | 0.515 | 99.49 | 98.73 |
| 11 | 0.080 | 0.640 | 0.090 | 0.960 | 0.330 | 2.100 | 97.90 | 98.64 |
| 12C | 0.390 | 0.460 | 0.560 | 0.350 | 1.060 | 2.820 | 97.18 | 98.46 |
| 13C | 0.056 | 0.527 | 0.518 | 0.154 | 0.107 | 1.362 | 98.64 | 98.39 |
| 14C | 0.941 | 0.298 | 0.051 | 0.001 | 0.696 | 1.987 | 98.01 | 98.32 |
| 15 | 0.348 | 0.043 | 0.095 | 0.411 | 0.011 | 0.908 | 99.09 | 98.20 |
| 16C | 0.322 | 0.005 | 0.311 | 0.567 | 0.061 | 1.267 | 98.73 | 98.14 |
| 17R | 0.510 | 0.850 | 0.190 | 0.420 | 0.750 | 2.720 | 97.28 | 98.01 |
| 18 | 0.411 | 0.322 | 0.259 | 1.079 | 0.604 | 2.676 | 97.32 | 97.90 |
| 19C | 0.086 | 0.162 | 0.067 | 0.164 | 0.018 | 0.496 | 99.50 | 97.77 |
| 21C | 0.108 | 0.804 | 0.363 | 0.137 | 0.196 | 1.609 | 98.39 | 97.70 |
| 22C | −1.573 | 0.163 | −3.812 | 0.926 | −4.622 | 11.097 | 88.90 | 97.47 |
| 23 | 0.168 | 0.246 | 0.214 | 0.346 | 0.146 | 1.118 | 98.88 | 97.32 |
| 25C | 0.240 | 0.110 | 0.110 | 0.280 | 0.260 | 1.000 | 99.00 | 97.28 |
| 26C | 0.612 | 0.820 | 0.349 | 0.558 | 0.525 | 2.864 | 97.14 | 97.18 |
| 27 | 0.820 | 0.850 | 0.090 | 0.020 | 1.600 | 3.380 | 96.62 | 97.14 |
| 28 | 0.331 | 0.129 | 0.439 | 0.063 | 0.837 | 1.799 | 98.20 | 97.14 |
| 30C | 0.720 | 0.530 | 0.180 | 0.360 | 1.070 | 2.860 | 97.14 | 96.62 |
| 31R | 0.202 | 0.095 | 0.111 | 0.237 | 0.019 | 0.665 | 99.34 | 96.46 |
| 32C | 0.446 | 0.292 | 1.434 | 0.784 | 1.388 | 4.344 | 95.66 | 95.66 |
| 33C | 0.680 | 0.770 | 0.780 | 1.480 | 2.170 | 5.880 | 94.12 | 94.12 |
| 34 | −1.650 | −3.060 | 0.700 | −6.530 | 2.520 | 14.460 | 85.54 | 93.00 |
| 35C | 0.044 | 0.083 | 0.058 | 0.021 | 0.039 | 0.245 | 99.76 | 88.90 |
| 36 | 0.380 | 0.170 | 0.110 | 0.490 | 1.150 | 2.300 | 97.70 | 85.54 |
| SD[b] | 0.42 | 0.43 | 0.47 | 0.58 | 0.96 | | | |

[a] Abbreviations: C, corrections applied; R, no corrections but response of detector checked; and —, values rejected (greater than 2 SD).
[b] Sum of the standard deviations, 2.86.

known, or standard deviation (means) = $\sqrt{\Sigma(d)^2/(n-1)}$ where d = deviation from means and n = number of collaborators. The sum of the standard deviations (ΣSD) of each component is shown in the Table. The value is a measure of the degree of accuracy of an analysis when a known mixture is analyzed or a measure of precision when an oil is analyzed. It is also valuable as a measure of the degree of difficulty of the analysis when comparing analyses of a number of oils. The sum is analogous to the standard deviation of the total determination and, therefore, indicates that about 68% of the collaborators should have a total deviation from the known values for each component of 2.86% or less. This is the total error in the analysis and when this percentage is subtracted from 100, the accuracy of the analysis is obtained. This is 97.14%, which is the minimum accuracy which should be attained by 68% of the collaborators. Actually, 22 of 31 collaborators have at least this grade, or 70.9%; two others in the Table appear to have attained this grade, but these are the result of rounding off of figures. The individual collaborator grades are obtained by subtracting their total deviation from 100. The grade is indicative of the correctness of the analysis. Arbitrarily, it was decided that analysts with a total deviation equal to or less than the sum of the standard deviations of all the components have made a good analysis. Analyses with a total deviation more than the sum, but not greater than twice the sum of the standard deviations are satisfactory. Analyses with a total deviation greater than twice the sum of the standard deviations are considered poor. This is analogous to differing by one, two, or more than two standard deviations.

Tables IV and V show similar data for the analysis of reference mixture D recommended by the National Institutes of Health (2) and designated as SGC 20 in this study. Again, the trimmed mean is in excellent agreement with the known values. The ΣSD of the sample is slightly greater than with mixture SGC 19. This would be expected, since the mixture contains a high percentage of polyunsaturated acids. In this analysis, five analysts failed to separate 18:3 from 20:0 (linolenic acid from arachidic acid). These values were not used in the determination of the standard deviation of each component, as indicated in the computer program above. However, they were used to calculate the collaborator's total deviation and, as a result, their grade for the analysis was low.

When oils are analyzed, the true composition is not known and the mean value for each component must be employed. However, when the trimmed mean values are so close to the known composition of two mixtures, as is demonstrated above, it is quite likely that they would also result in values close to the true composition of an oil.

TABLE IV

Normalized Fatty Acid Analysis; SGC 20 Me Ester Mixture AOCS Smalley Gas Chromatography Series, 1968–69

| Laboratory | 16:0, % | 18:0, % | 18:1, % | 18:2, % | 18:3, % | 20:0, % |
|---|---|---|---|---|---|---|
| 2C[a] | 6.05 | 3.00 | 34.91 | 50.02 | 2.99 | 3.03 |
| 3C | 6.27 | 2.70 | 35.08 | 49.15 | 3.38 | 3.43 |
| 5C | 6.12 | 3.03 | 35.53 | 49.18 | X6.13 | X0.00 |
| 6C | 5.35 | 2.50 | 35.06 | 50.76 | 3.23 | 3.10 |
| 7C | 6.04 | 2.81 | 33.49 | 51.61 | 3.40 | 2.65 |
| 8R | 6.63 | 3.03 | 36.43 | 49.33 | 1.88 | 2.71 |
| 9R | 6.24 | 2.70 | 34.40 | 51.39 | X5.27 | X0.00 |
| 10 | 5.92 | 3.09 | 34.93 | 50.21 | 2.76 | 3.09 |
| 11 | 5.75 | 2.95 | 34.08 | 50.72 | 3.10 | 3.40 |
| 12C | 5.77 | 2.89 | 35.05 | 50.25 | 2.95 | 3.09 |
| 13C | 5.59 | 2.56 | −30.05 | −54.99 | 3.77 | 3.04 |
| 14C | 5.81 | 2.84 | 33.96 | 51.50 | 3.03 | 2.86 |
| 15 | 6.05 | 3.00 | 35.42 | 49.86 | 2.60 | 3.07 |
| 16C | 5.89 | 2.95 | 34.75 | 50.21 | 3.23 | 2.97 |
| 17R | 6.23 | 2.89 | 36.50 | 49.00 | 2.29 | 3.09 |
| 18 | 6.18 | 3.18 | 35.74 | 50.07 | 2.26 | 2.57 |
| 19C | −4.83 | 2.45 | −29.71 | −56.59 | 3.77 | 2.65 |
| 21C | 5.76 | 2.87 | 34.20 | 50.06 | 3.79 | 3.32 |
| 22C | 6.48 | 3.77 | 34.67 | 47.38 | X7.71 | X0.00 |
| 23 | 6.16 | 3.08 | 35.18 | 48.76 | 3.09 | 3.73 |
| 25C | 5.87 | 2.84 | 33.13 | 51.01 | X7.15 | X0.00 |
| 26C | 6.17 | 2.91 | 34.80 | 49.88 | 3.27 | 2.97 |
| 27 | 6.78 | 3.00 | 36.32 | 48.75 | 2.86 | 2.29 |
| 28 | 6.41 | 2.88 | 35.72 | 49.92 | 2.22 | 2.85 |
| 30C | 6.13 | 2.82 | 35.34 | 50.09 | X5.62 | X0.00 |
| 31R | 6.07 | 2.99 | 35.71 | 49.48 | 2.76 | 3.00 |
| 32C | 6.02 | 3.40 | −30.87 | 49.86 | −4.46 | −5.40 |
| 33C | −7.82 | 2.86 | 34.47 | 48.85 | 3.32 | 2.68 |
| 34 | 6.89 | −0.60 | −39.25 | 49.69 | −0.85 | 2.72 |
| 35C | 5.82 | 2.87 | 34.62 | 50.31 | 3.29 | 3.08 |
| 36 | 5.90 | 2.99 | 34.41 | 50.28 | 3.23 | 3.19 |
| Trimmed means | 6.09 | 2.93 | 35.00 | 49.97 | 3.02 | 2.99 |
| Known values | 6.04 | 3.05 | 34.92 | 49.86 | 3.06 | 3.06 |
| Difference | 0.05 | 0.12 | 0.08 | 0.11 | 0.04 | 0.07 |

[a] Abbreviations, C, corrections applied; R, no corrections but response of detector checked; —, values rejected (to obtain trimmed mean); and X, values rejected (overlapped peaks, 18:3 and 20:0).

TABLE V

Deviations and Grades; SGC 20 Me Ester Mixture AOCS Smalley Gas Chromatography Series, 1968–69

| Laboratory | 16:0, % | 18:0, % | 18:1, % | 18:2, % | 18:3, % | 20:0, % | Tot. dev., % | Grade, % | Ordered grades, % |
|---|---|---|---|---|---|---|---|---|---|
| 2C[a] | 0.008 | 0.051 | 0.010 | 0.155 | 0.071 | 0.031 | 0.326 | 99.67 | 99.67 |
| 3C | 0.227 | 0.351 | 0.153 | 0.715 | 0.318 | 0.368 | 2.133 | 97.87 | 99.27 |
| 5C | 0.078 | 0.021 | 0.610 | 0.675 | X3.069 | X3.061 | 7.514 | 92.49 | 99.16 |
| 6C | 0.692 | 0.551 | 0.140 | 0.895 | 0.169 | 0.039 | 2.486 | 97.51 | 98.97 |
| 7C | 0.003 | 0.242 | 1.437 | 1.755 | 0.338 | 0.411 | 4.187 | 95.81 | 98.97 |
| 8R | 0.583 | 0.023 | 1.511 | 0.534 | 1.183 | 0.353 | 4.187 | 95.81 | 98.91 |
| 9R | 0.197 | 0.351 | 0.527 | 1.535 | X2.208 | X3.061 | 7.880 | 92.12 | 98.60 |
| 10 | 0.121 | 0.039 | 0.003 | 0.350 | 0.301 | 0.029 | 0.844 | 99.16 | 98.57 |
| 11 | 0.295 | 0.103 | 0.841 | 0.865 | 0.037 | 0.337 | 2.478 | 97.52 | 98.38 |
| 12C | 0.272 | 0.161 | 0.126 | 0.390 | 0.111 | 0.029 | 1.090 | 98.91 | 97.87 |
| 13C | 0.452 | 0.491 | −4.874 | −5.130 | 0.709 | 0.021 | 11.678 | 88.32 | 97.80 |
| 14C | 0.235 | 0.213 | 0.961 | 1.644 | 0.033 | 0.203 | 3.289 | 96.71 | 97.63 |
| 15 | 0.006 | 0.052 | 0.499 | 0.000 | 0.462 | 0.008 | 1.027 | 98.97 | 97.55 |
| 16C | 0.149 | 0.100 | 0.177 | 0.345 | 0.170 | 0.090 | 1.031 | 98.97 | 97.52 |
| 17R | 0.188 | 0.161 | 1.576 | 0.860 | 0.771 | 0.029 | 3.585 | 96.42 | 97.51 |
| 18 | 0.138 | 0.129 | 0.816 | 0.210 | 0.801 | 0.491 | 2.585 | 97.42 | 97.42 |
| 19C | −1.212 | 0.601 | −5.217 | −6.730 | 0.710 | 0.409 | 14.880 | 85.12 | 96.71 |
| 21C | 0.280 | 0.180 | 0.727 | 0.195 | 0.731 | 0.260 | 2.372 | 97.63 | 96.42 |
| 22C | 0.437 | 0.718 | 0.257 | 2.485 | X4.648 | X3.061 | 11.607 | 88.39 | 95.93 |
| 23 | 0.118 | 0.029 | 0.256 | 1.100 | 0.029 | 0.669 | 2.200 | 97.80 | 95.81 |
| 25C | 0.172 | 0.211 | 1.794 | 1.150 | X4.089 | X3.061 | 10.478 | 89.52 | 95.81 |
| 26C | 0.132 | 0.145 | 0.124 | 0.025 | 0.206 | 0.094 | 0.726 | 99.27 | 95.73 |
| 27 | 0.738 | 0.051 | 1.396 | 1.110 | 0.201 | 0.771 | 4.267 | 95.73 | 93.42 |
| 28 | 0.368 | 0.171 | 0.796 | 0.060 | 0.841 | 0.211 | 2.447 | 97.55 | 92.49 |
| 30C | 0.088 | 0.231 | 0.420 | 0.225 | X2.559 | X3.061 | 6.584 | 93.41 | 92.12 |
| 31R | 0.023 | 0.064 | 0.785 | 0.376 | 0.304 | 0.064 | 1.616 | 98.38 | 91.83 |
| 32C | 0.023 | 0.348 | −4.057 | 0.005 | −1.398 | −2.338 | 8.170 | 91.83 | 89.65 |
| 33C | −1.778 | 0.191 | 0.454 | 1.010 | 0.259 | 0.381 | 4.073 | 95.93 | 89.52 |
| 34 | 0.848 | −2.451 | −4.326 | 0.170 | −2.211 | 0.341 | 10.347 | 89.65 | 88.39 |
| 35C | 0.224 | 0.177 | 0.302 | 0.446 | 0.234 | 0.023 | 1.405 | 98.60 | 88.32 |
| 36 | 0.142 | 0.061 | 0.511 | 0.415 | 0.169 | 0.129 | 1.427 | 98.57 | 85.12 |
| SD[b] | 0.33 | 0.27 | 0.82 | 0.90 | 0.49 | 0.31 | | | |

[a] Abbreviations: C, corrections applied; R, no corrections but response of detector checked; —, values rejected (greater than 2 SD); and X, values rejected (overlapped peaks 18:3 and 20:0).
[b] Sum of the standard deviations, 3.13.

TABLE VI

Fatty Acid Analysis; SGC 10 Safflower Oil AOCS Smalley Gas Chromatography Series, 1966–67

| Lab. | 14:0, % | 16:0, % | 16:1, % | 18:0, % | 18:1, % | 18:2, % | 20:0, % | 18:3, % | Tot. dev., % |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.07 | 6.48 | 0.25 | 2.36 | 10.68 | 79.75 | 0.22 | 0.19 | 4.10 |
| 3 | 0.09 | 6.74 | 0.00 | 2.98 | 12.14 | 77.74 | 0.31 | 0.00 | 1.54 |
| 4C[a] | 0.21 | 8.88 | 0.79 | 3.44 | 15.44 | 69.37 | 0.33 | 1.54 | 16.87 |
| 6 | 0.13 | 7.34 | 0.14 | 3.24 | 12.41 | 76.29 | 0.45 | 0.00 | 3.85 |
| 7 | 0.09 | 7.28 | 0.15 | 2.45 | 11.97 | 77.95 | 0.04 | 0.06 | 1.83 |
| 8 | 0.09 | 6.84 | 0.28 | 2.83 | 11.86 | 76.73 | 0.91 | 0.46 | 2.20 |
| 10C | 0.11 | 6.30 | 0.12 | 2.56 | 11.06 | 79.00 | 0.36 | 0.49 | 2.61 |
| 12C | 0.00 | 6.16 | 0.00 | 2.83 | 11.16 | 79.85 | 0.00 | 0.00 | 4.37 |
| 13 | 0.04 | 6.58 | 0.03 | 2.60 | 11.75 | 78.37 | 0.28 | 0.35 | 1.34 |
| 14 | 0.08 | 7.13 | 0.01 | 2.68 | 11.79 | 77.82 | 0.00 | 0.49 | 1.05 |
| 15C | 0.15 | 7.15 | 0.16 | 2.63 | 11.51 | 77.87 | 0.24 | 0.29 | 0.84 |
| 17 | 0.00 | 7.91 | 0.00 | 3.00 | 12.78 | 76.31 | 0.00 | 0.00 | 4.99 |
| 18 | 0.00 | 6.57 | 0.00 | 2.61 | 11.45 | 79.37 | 0.00 | 0.00 | 3.13 |
| 19 | 0.00 | 6.87 | 0.00 | 2.14 | 11.11 | 79.88 | 0.00 | 0.00 | 4.21 |
| 20 | 0.25 | 6.92 | 0.24 | 2.90 | 12.08 | 76.26 | 0.72 | 0.64 | 3.09 |
| 21 | 0.17 | 6.76 | 0.00 | 2.43 | 11.22 | 78.71 | 0.00 | 0.71 | 2.52 |
| 23 | 0.00 | 8.73 | 0.00 | 3.31 | 12.66 | 75.30 | 0.00 | 0.00 | 7.01 |
| 25 | 0.10 | 7.03 | 0.12 | 2.66 | 11.75 | 77.48 | 0.35 | 0.51 | 0.81 |
| 27 | 0.00 | 6.66 | 0.00 | 2.70 | 11.46 | 79.18 | 0.00 | 0.00 | 2.77 |
| 28 | 0.17 | 6.91 | 0.21 | 2.54 | 11.48 | 78.16 | 0.25 | 0.28 | 1.09 |
| 29 | 0.10 | 6.90 | 0.09 | 2.68 | 11.49 | 78.01 | 0.40 | 0.34 | 0.66 |
| 30C | 0.13 | 6.70 | 0.14 | 2.63 | 11.50 | 77.95 | 0.39 | 0.55 | 0.72 |
| Trimmed means | 0.12 | 6.84 | 0.15 | 2.70 | 11.65 | 77.80 | 0.33 | 0.41 | |
| SD[b] | 0.04 | 0.39 | 0.08 | 0.28 | 0.53 | 1.30 | 0.15 | 0.18 | |

[a] C, corrections applied.
[b] Sum of the standard deviations, 2.97.

TABLE VII

Fatty Acid Analysis; SGC 17 Soybean Oil AOCS Smalley Gas Chromatography Series, 1967–68

| Lab. | 14:0, % | 16:0, % | 18:0, % | 18:1, % | 18:2, % | 18:3, % | Tot. dev., % |
|---|---|---|---|---|---|---|---|
| 3 | 0.00 | 8.30 | 3.37 | 48.18 | 36.28 | 3.86 | 3.86 |
| 4C[a] | 0.06 | 8.87 | 3.94 | 45.40 | 38.70 | 3.03 | 5.95 |
| 5 | 0.09 | 9.40 | 3.90 | 48.68 | 35.40 | 2.53 | 2.34 |
| 6C | 0.00 | 8.77 | 3.95 | 47.58 | 36.74 | 2.96 | 1.92 |
| 8 | 0.18 | 13.07 | 7.29 | 44.11 | 35.35 | 0.00 | 13.88 |
| 9C | 0.00 | 9.34 | 3.71 | 48.06 | 36.16 | 2.73 | 1.72 |
| 11C | 0.00 | 8.92 | 3.97 | 48.10 | 35.74 | 3.28 | 1.52 |
| 12C | 0.00 | 10.62 | 6.02 | 41.73 | 36.82 | 4.81 | 12.00 |
| 13R | 0.06 | 9.34 | 4.78 | 50.66 | 32.57 | 2.60 | 7.22 |
| 14 | 0.00 | 9.76 | 4.22 | 48.32 | 34.93 | 2.76 | 2.34 |
| 15C | 0.00 | 9.54 | 4.48 | 48.07 | 34.94 | 2.97 | 1.87 |
| 16 | 0.08 | 8.82 | 4.04 | 47.54 | 36.25 | 3.27 | 1.53 |
| 17C | 0.07 | 9.22 | 4.11 | 49.53 | 34.54 | 2.54 | 3.76 |
| 18C | 0.05 | 8.52 | 3.80 | 47.80 | 36.92 | 2.91 | 2.58 |
| 19R | 0.31 | 9.47 | 4.84 | 50.41 | 34.98 | 0.00 | 7.55 |
| 20C | 0.00 | 8.62 | 4.33 | 51.35 | 33.48 | 2.22 | 7.58 |
| 21 | 0.14 | 9.08 | 2.81 | 47.61 | 36.51 | 3.85 | 3.33 |
| 24 | 0.00 | 10.19 | 3.64 | 44.85 | 36.46 | 4.86 | 6.98 |
| 26C | 0.14 | 12.30 | 6.36 | 45.38 | 35.82 | 0.00 | 10.48 |
| 27R | 0.03 | 9.08 | 4.21 | 48.98 | 34.82 | 2.88 | 2.67 |
| 28R | 0.03 | 8.66 | 4.00 | 48.13 | 36.04 | 3.14 | 1.83 |
| 29 | 0.09 | 8.32 | 3.49 | 47.05 | 37.47 | 3.58 | 4.60 |
| 30C | 0.07 | 9.60 | 4.02 | 47.83 | 36.04 | 2.43 | 1.55 |
| 31 | 0.10 | 14.96 | 6.38 | 67.47 | 10.94 | 0.15 | 55.33 |
| 32 | 0.00 | 9.76 | 3.21 | 48.84 | 36.56 | 1.63 | 4.92 |
| 33 | 0.00 | 9.02 | 5.16 | 48.43 | 34.68 | 2.71 | 3.39 |
| 34C | 0.00 | 8.47 | 3.82 | 47.70 | 37.30 | 2.71 | 3.14 |
| Trimmed means | 0.09 | 9.27 | 4.25 | 47.65 | 35.78 | 2.97 | |
| SD[b] | 0.04 | 0.85 | 0.89 | 2.06 | 1.28 | 0.65 | |

[a] C, corrections applied; R, no corrections but response of detector checked.
[b] Sum of the standard deviations, 5.78.

TABLE VIII

Fatty Acid Analysis; SGC 14 Coconut Oil AOCS Smalley Gas Chromatography Series, 1967–68

| Lab. | 6:0, % | 8:0, % | 10:0, % | 12:0, % | 14:0, % | 16:0, % | 18:0, % | 18:1, % | 18:2, % | Tot. Dev. % |
|---|---|---|---|---|---|---|---|---|---|---|
| 2C[a] | 0.57 | 8.11 | 6.38 | 47.71 | 17.16 | 8.04 | 2.70 | 8.40 | 0.94 | 4.86 |
| 4C | 0.00 | 9.09 | 6.55 | 47.63 | 17.05 | 8.27 | 2.54 | 6.32 | 2.56 | 4.49 |
| 5 | 0.19 | 7.62 | 6.77 | 48.69 | 17.57 | 8.47 | 2.61 | 6.11 | 1.97 | 3.59 |
| 6R | 0.54 | 8.21 | 6.45 | 46.65 | 17.46 | 8.72 | 2.71 | 6.86 | 2.40 | 1.86 |
| 8R | 0.00 | 4.57 | 5.43 | 43.30 | 21.83 | 11.07 | 3.34 | 8.30 | 2.16 | 17.64 |
| 9C | 0.76 | 9.81 | 6.87 | 46.24 | 16.89 | 8.60 | 2.47 | 6.35 | 2.02 | 5.20 |
| 11C | 0.74 | 9.22 | 6.46 | 48.22 | 16.64 | 8.15 | 2.50 | 5.99 | 2.09 | 5.03 |
| 13 | 0.00 | 5.67 | 5.38 | 47.12 | 20.24 | 10.62 | 2.79 | 6.67 | 1.50 | 9.19 |
| 14 | 0.00 | 8.47 | 6.29 | 45.80 | 17.35 | 8.87 | 2.91 | 7.26 | 3.05 | 5.01 |
| 15C | 0.80 | 7.96 | 6.96 | 46.57 | 17.42 | 8.11 | 2.72 | 6.84 | 2.62 | 3.07 |
| 16 | 1.25 | 9.07 | 6.74 | 46.95 | 16.84 | 8.29 | 2.54 | 6.15 | 2.18 | 4.57 |
| 17 | 0.00 | 14.77 | 9.34 | 49.32 | 15.84 | 4.24 | 1.49 | 3.44 | 1.58 | 23.92 |
| 18C | 0.00 | 12.54 | 6.74 | 45.00 | 16.57 | 8.09 | 2.54 | 6.34 | 2.19 | 10.35 |
| 19R | 0.22 | 5.90 | 5.02 | 43.72 | 19.86 | 10.60 | 3.51 | 8.40 | 2.78 | 14.53 |
| 20C | 0.00 | 3.35 | 4.66 | 46.78 | 19.73 | 10.85 | 3.46 | 8.54 | 1.64 | 14.68 |
| 24C | 0.00 | 7.63 | 6.68 | 45.03 | 17.64 | 8.62 | 2.89 | 7.83 | 3.69 | 6.40 |
| 25 | 1.71 | 6.42 | 3.42 | 49.66 | 18.41 | 8.77 | 2.78 | 6.85 | 1.97 | 8.96 |
| 27R | 0.60 | 6.05 | 4.89 | 48.72 | 17.78 | 8.83 | 3.49 | 7.40 | 2.25 | 6.60 |
| 28R | 1.60 | 7.84 | 6.42 | 47.58 | 17.91 | 8.70 | 2.30 | 6.15 | 1.51 | 3.23 |
| 29 | 0.00 | 9.08 | 7.10 | 48.59 | 17.02 | 7.89 | 2.33 | 5.96 | 2.04 | 6.61 |
| 30C | 0.48 | 9.21 | 6.96 | 46.65 | 17.72 | 8.40 | 2.43 | 6.06 | 2.08 | 4.20 |
| 31 | 0.43 | 8.90 | 7.38 | 52.71 | 16.85 | 6.60 | 1.66 | 4.20 | 1.27 | 15.05 |
| 32 | 0.37 | 6.80 | 6.22 | 48.72 | 18.08 | 8.88 | 2.56 | 6.32 | 2.05 | 4.09 |
| 33 | 0.00 | 4.38 | 6.78 | 53.43 | 16.66 | 8.24 | 2.82 | 5.90 | 1.78 | 13.32 |
| 34C | 0.00 | 10.56 | 7.21 | 49.17 | 16.60 | 7.36 | 2.09 | 5.20 | 1.81 | 10.96 |
| *Trimmed means* | 0.66 | 7.80 | 6.38 | 47.28 | 17.61 | 8.74 | 2.70 | 6.71 | 2.12 | |
| SD[b] | 0.39 | 2.10 | 0.76 | 1.73 | 1.09 | 1.08 | 0.44 | 1.06 | 0.44 | |

[a] C, corrections applied; R, no corrections but response of detector checked.
[b] Sum of the standard deviations, 9.09.

Tables VI, VII and VIII show the complete data for the analysis of several oils analyzed by the AOCS Smalley collaborators. Safflower oil is an example of an easily determined oil, soybean oil, an average oil, and coconut oil is an example of oil which is analyzed with difficulty. The averages of duplicates are given for component fatty acids along with the trimmed mean, the standard deviation of each component, the sum of the standard deviations of each sample, and the total deviation for each laboratory. In all figures, the letters accompanying the laboratory number stand for the following: C indicates that calibration factors have been employed, R indicates that response of the detector has been checked (it was decided that calibration factors were not necessary), while no letter indicates that no factors were used and the detector response was not checked. When the first oil was analyzed (SGC 9, cottonseed), only six collaborators employed calibration factors, while only five collaborators did not use factors or check their response when the most recent oil (SGC 24, linseed) was analyzed. Tables IX and X show the composition of the fatty acids for various other oils as determined from the trimmed means and the standard deviations for each acid.

In the calculations applied to the data, all values over 2 SD are discarded in the calculation of the trimmed means. Therefore, when comparing the collaborator's total deviation with the final ΣSD, we would expect 68.3% of the remaining 95.5% collaborators, or 65.2% (95.5 × .683), to have a good analysis, and 91.2% (95.5 × .955) to have an acceptable analysis. For certain oils these figures will not hold since additional collaborator's values are rejected in the calculation of the trimmed means when overlapping peaks are unresolved. In general, however, these are the approximate percentages found. A collaborator, by comparing his total deviation with the ΣSD, can immediately determine whether he has made a good, satisfactory or poor analysis, using the standards suggested by this treatment of the data. The ΣSD will also reveal the degree of difficulty in analyzing the oil. From the data, good analyses of the oils range from an error of up to 3.0% (ΣSD) in the determination of the means for safflower oil to an error of 9.1% (ΣSD) for coconut oil. Satisfactory analyses for the same oils range from an error of 5.9% (2 × ΣSD) aand 18.2% (2 × ΣSD), respectively. Much of the error in the analysis of coconut oil can be attributed to the presence of short chain acids which are lost or partially lost in the conversion to methyl esters.

It has been suggested that, when a method is subjected to collaborative study to determine how good it is, the collaborators should be screened by determining how well they could analyze a known sample, and only those agreeing within certain limits should be chosen for testing the method. Eight collaborators,

TABLE IX

Fatty Acid Analyses of Various Oils AOCS Smalley Gas Chromatography Series

| Fatty acid | Cottonseed oil SGC 22 | | Cottonseed oil SGC 9 | | Olive oil SGC 16 | | Lard SGC 21 | | Peanut oil SGC 13 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Trimmed mean, % | SD, % | Trimmed mean, % | SD, % | Trimmed mean, % | SD, % | Trimmed mean, % | SD, % | Trimmed mean, % | SD, % |
| 10:0 | ..... | ..... | ..... | ..... | ..... | ..... | 0.08 | 0.04 | ..... | ..... |
| 12:0 | ..... | ..... | ..... | ..... | ..... | ..... | 0.09 | 0.04 | 1.01 | 0.16 |
| 14:0 | 0.74 | 0.09 | 0.85 | 0.11 | ..... | ..... | 1.40 | 0.13 | 0.39 | 0.07 |
| 16:0 | 20.45 | 0.81 | 23.56 | 0.95 | 11.90 | 0.66 | 25.14 | 0.52 | 9.75 | 0.43 |
| 16:1 | 0.64 | 0.17 | 0.63 | 0.18 | 1.00 | 0.17 | 2.88 | 0.28 | ..... | ..... |
| 17:0 | ..... | ..... | ..... | ..... | ..... | ..... | 0.35 | 0.11 | ..... | ..... |
| 17:1 | ..... | ..... | ..... | ..... | ..... | ..... | 0.27 | 0.10 | ..... | ..... |
| 18:0 | 2.46 | 0.31 | 2.33 | 0.23 | 3.06 | 0.42 | 13.84 | 0.83 | 2.63 | 0.30 |
| 18:1 | 18.45 | 0.65 | 17.64 | 0.77 | 74.63 | 1.34 | 44.80 | 0.74 | 51.58 | 1.33 |
| 18:2 | 57.28 | 1.34 | 54.31 | 1.00 | 8.38 | 0.96 | 10.19 | 0.67 | 26.97 | 1.31 |
| 18:3 | ..... | ..... | 0.36 | 0.24 | 0.68 | 0.16 | 0.97 | 0.46 | ..... | ..... |
| 20:0 | ..... | ..... | 0.32 | 0.19 | 0.35 | 0.16 | ..... | ..... | 1.39 | 0.26 |
| 20:1 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | 1.52 | 0.26 |
| 22:0 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | 3.33 | 0.36 |
| 24:0 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | 1.43 | 0.51 |

TABLE X

Fatty Acid Analyses of Various Oils AOCS Smalley Gas Chromatography Series

| Fatty acid | Tall oil SGC 15 | | Linseed oil SGC 24 | | Corn oil SGC 18 | | Rapeseed oil SGC 12 | | Rapeseed oil SGC 23 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Trimmed mean, % | SD, % | Trimmed mean, % | SD, % | Trimmed mean, % | SD, % | Trimmed mean, % | SD, % | Trimmed mean, % | SD, % |
| 14:0 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... | 0.06 | 0.02 |
| 16:0 | ..... | ..... | 6.01 | 0.48 | 11.64 | 1.26 | 3.07 | 0.30 | 3.09 | 0.19 |
| 16:1 | ..... | ..... | ..... | ..... | ..... | ..... | 0.21 | 0.10 | 0.21 | 0.09 |
| 18:0 | 2.74 | 0.49 | 4.05 | 0.57 | 2.16 | 0.46 | 1.18 | 0.13 | 1.27 | 0.28 |
| 18:1 | 52.94 | 1.76 | 19.70 | 1.08 | 26.78 | 1.33 | 14.75 | 1.09 | 16.18 | 0.92 |
| 18:2 | 37.61 | 1.39 | 15.29 | 0.78 | 57.98 | 2.82 | 15.88 | 0.69 | 16.63 | 0.96 |
| 18:3 | ..... | ..... | 54.95 | 3.22 | 0.89 | 0.35 | 10.31 | 0.52 | 11.02 | 0.84 |
| 20:0 | ..... | ..... | ..... | ..... | 0.55 | 0.26 | 0.72 | 0.11 | 0.70 | 0.17 |
| 20:1 | ..... | ..... | ..... | ..... | ..... | ..... | 9.29 | 0.74 | 10.03 | 0.53 |
| 20:2 | ..... | ..... | ..... | ..... | ..... | ..... | 0.68 | 0.16 | 0.66 | 0.23 |
| 22:0 | ..... | ..... | ..... | ..... | ..... | ..... | 0.45 | 0.19 | 0.48 | 0.25 |
| 22:1 | ..... | ..... | ..... | ..... | ..... | ..... | 41.52 | 2.35 | 38.03 | 2.33 |
| 22:2 | ..... | ..... | ..... | ..... | ..... | ..... | 0.77 | 0.52 | 0.54 | 0.31 |
| 24:1 | ..... | ..... | ..... | ..... | ..... | ..... | 1.17 | 0.67 | 1.09 | 0.57 |
| Conj. 18:2, C-C | 0.97 | 0.26 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| Conj. 18:2, C-T | 2.40 | 0.48 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| Conj. 18:2, T-T | 1.82 | 0.56 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| ? | 1.52 | 0.69 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |

who had analyzed all samples and scored well, were singled out and the sum of the standard deviations of the sample determined for this group. A comparison of all collaborators with this select group is shown in Table XI. Calculated values are also shown. The method for the calculation of these will be explained later in the text. The order of difficulty in analyzing an oil is reflected in the ΣSD of the sample. The oils are listed in the Table in the order of increasing difficulty, as determined by the data from all collaborators. The order of difficulty for the select group and the total group differ, but the order for the select group should be more accurate because of their selection. This difference is probably due to more experience and possibly overall care in analyzing the sample. Again, considering that results within 2 × ΣSD are indicative of a satisfactory analysis and that the adjusted mean is the true composition, the select group has an error of 3.5% (2 × ΣSD) for the analysis of safflower oil compared to an error of 5.9% for the total group. Coconut oil was analyzed by the select group with an error of 12.4%, whereas the total group had an error of 18.2%.

The data for all the oils were used to determine an average coefficient of variation (c.v. = SD/means × 100) for differing percentages of methyl palmitate, methyl stearate, methyl oleate and methyl linolenate. The coefficients for these components were reasonably close at equivalent percentage levels. Therefore, the data were combined to obtain average values. The total curve is shown in Figure 1. Typical average c.v. values are 1% = 16.5; 5% = 10.7; 10% = 7.2; 20% = 4.1; 30% = 3.1; 40% = 2.8; 60% = 2.2; 80% = 1.8. The curve shown in Figure 1 can be used as a guide to determine the approximate error expected for the analysis of an oil in the following manner: c.v. × means/100 = SD. Using c.v. from the curve and the determined percentage of each component of any mixture as the means, the calculation will be the approximate SD and the ΣSD should approximate those determined by all the collaborators. Shown in Table XI are values calculated in this manner. Many agree well with the experimental data. Most of those which do not can be explained in one way or another. For example, SGC 14, coconut oil has an experimental value of 9.09, but the calculated value is 5.47. Because of the short chain acids present in this oil, many collaborators lost a portion in the methylation procedure and thus, for this oil, they had a relatively large standard deviation for each component compared to the average of all oils. This would result in a large difference. SGC 12 and 23 are both rapeseed oils. This oil contains a number of components with a retention time greater than the $C_{18}$ acids. The peaks representing these acids are usually broad and of small height on the chromatogram. These peaks are difficult to measure; again the standard deviations are greater than the averages given and result in larger values than calculated. But the calculated standard

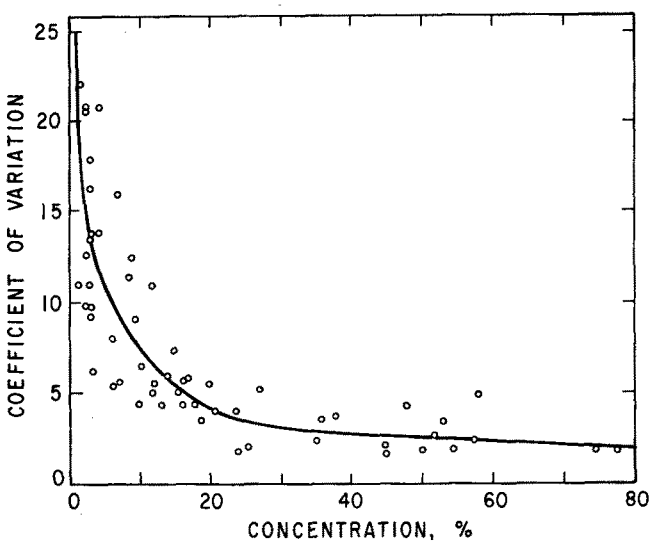


FIG. 1. Composite coefficient of variation curve.

TABLE XI

Relative Difficulty of Analysis

| Sample | Sum of SD of each acid | | |
|---|---|---|---|
| | All collaborators, % | Select group,[a] % | Calculated, % |
| SGC 10 Safflower oil (22)[b] | 2.97 | 1.73 | 3.33 |
| SGC 22 Cottonseed oil (28) | 3.38 | 2.19 | 3.66 |
| SGC 9 Cottonseed oil (24) | 3.69 | 2.82 | 3.72 |
| SGC 16 Olive oil (26) | 3.87 | 2.85 | 3.70 |
| SGC 21 Lard (28) | 3.91 | 3.40 | 4.77 |
| SGC 13 Peanut oil (24) | 5.00 | 3.06 | 4.60 |
| SGC 15 Tall oil (24) | 5.64 | 4.86 | 3.61 |
| SGC 17 Soybean oil (27) | 5.78 | 4.10 | 3.98 |
| SGC 24 Linseed oil (27) | 6.14 | 2.57 | 4.07 |
| SGC 18 Corn oil (27) | 6.48 | 2.80 | 3.53 |
| SGC 12 Rapeseed oil (22) | 7.58 | 4.65 | 5.47 |
| SGC 23 Rapeseed oil (27) | 7.71 | 5.01 | 5.49 |
| SGC 14 Coconut oil (25) | 9.09 | 6.19 | 5.47 |
| SGC 19 Me ester mixture (31) | 2.86 | 2.30 | 4.12 |
| SGC 20 Me ester mixture (31) | 3.13 | 2.87 | 4.09 |

[a] Eight collaborators (see text).
[b] Figures in parentheses are the total number of collaborators.

TABLE XII

Comparison of Fatty Acid Analysis Using Thermal Conductivity or Flame Ionization Detectors

| Acids[a] | SGC 9 Cottonseed | | | | SGC 10 Safflower | | | |
|---|---|---|---|---|---|---|---|---|
| | Mean[b] | | SD | | Mean[c] | | SD | |
| | TC, % | FI, % | TC, % | FI, % | TC, % | FI, % | TC, % | FI, % |
| 14:0 | 0.83 | 0.88 | 0.12 | 0.10 | 0.12 | 0.13 | 0.03 | 0.06 |
| 16:0 | 23.85 | 23.16 | 0.98 | 0.85 | 6.92 | 6.77 | 0.49 | 0.21 |
| 16:1 | 0.62 | 0.66 | 0.18 | 0.19 | 0.15 | 0.15 | 0.08 | 0.07 |
| 18:0 | 2.24 | 2.39 | 0.23 | 0.23 | 2.74 | 2.78 | 0.32 | 0.35 |
| 18:1 | 17.43 | 17.79 | 0.62 | 0.72 | 11.73 | 11.67 | 0.59 | 0.62 |
| 18:2 | 54.35 | 54.39 | 1.03 | 0.99 | 77.55 | 77.66 | 1.51 | 1.35 |
| 18:3 | 0.31 | 0.45 | 0.11 | 0.40 | 0.39 | 0.43 | 0.28 | 0.17 |
| 20:0 | 0.37 | 0.28 | 0.17 | 0.20 | 0.40 | 0.41 | 0.18 | 0.21 |
| ΣS.D. | | | 3.44 | 3.68 | | | 3.48 | 3.04 |

[a] Number to left indicates carbon number; number to right indicates double bonds.
[b] TC used by 14 collaborators; FI by 10 collaborators.
[c] TC used by 12 collaborators; FI by 11 collaborators.

deviation does give a reasonable guide to the degree of accuracy one might expect to have for any sample, provided the analysis was determined with at least average care.

In an earlier report (3) it was indicated that when using a flame ionization detector, the precision was not as good as that obtained with the use of a thermal conductivity detector. Subsequently it was reported that this difference had been eliminated (1). Table XII shows a comparison of two oils analyzed by chromatographs employing these two detectors. These two oils, SGC 9 (cottonseed) and SGC 10 (safflower) are compared because the number of collaborators using each type of detector are nearly equal. The differences in the sum of the standard deviation are not considered significant and substantiate the observation that differences have been eliminated.

Employing the procedure presented to determine the collaborators' total deviation, it would seem possible for any analyst to compare his analyses with those obtained by the AOCS Smalley collaborators. This could be done by comparing their analysis of the known mixtures (SGC 19 and SGC 20, which are available commercially) with the group analysis in the following manner: (a) Analyze the known mixture. (b) Calculate the deviation from the known composition. (c) Sum the deviations of each component. (d) Compare this value with the sum of the standard deviations of the known mixture obtained by the AOCS Smalley collaborators.

If the observed total deviation is no greater than $2 \times \Sigma SD$ obtained by the collaborators, it is probable that the accuracy of their analysis of comparable oils would be expected to fall within $2 \times \Sigma SD$ found by the collaborators for that particular oil.

The statistical procedure presented here should have application to most collaborative studies involving gas liquid chromatography.

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