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Analog-Computer Program for Resolution of Overlapping Distribution Curves*

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Summary

A program to generate overlapping distribution functions was written for an analog computer. The position, width, amplitude, and skewing of each function can be varied to match experimental data. Component percentages can be calculated from integral curves. Special features of the system are: Matching can be done rapidly by using an oscilloscope, only standard equipment is needed, and parameters of the distribution are related to potentiometer settings.

Overlapping distribution curves are frequently encountered in physical, biological, and social sciences. In analytical chemistry, gas-chromatographic curves, countercurrent distributions, and data from mass, infrared, and nuclear magnetic resonance spectrometers illustrate the occurrence and frequent need for resolving overlapping peaks into component distribution curves. An electromechanical apparatus for performing this resolving operation has been described by French (*4*).

Oscilloscopic presentation of data is particularly helpful for curve fitting. Individual component distribution curves are adjusted on

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the screen until their summation approximates the experimental data. Such oscilloscopic readout from multiple function generators has been described by Abel and Noble (*1*). Their method is not adaptable to general-purpose analog computers since component distributions are formed empirically by shaping triangular input signals and by exploiting the nonlinear characteristics of heavily loaded vacuum tubes.

A more rigorous analytic basis underlies the method described by Brusenbach (*2*), which programs a general-purpose analog computer for the differential of the normal frequency curve; $y' = [-(t - u)/\sigma^2]y$. A similarly based program was written and tested independently in our laboratory; however, repetitive operation and oscilloscopic presentation of data were not feasible because of problems inherent in reproducible setting of initial conditions. This approach was subsequently dropped in favor of the procedure described here, which generates the gaussian equation directly and which is amenable to oscillographic presentation as well as to normal recording.

PROGRAM

Generation of four normal frequency-distribution curves is accomplished by the program shown in Fig. 1, written for a 10-V Pace TR-48 analog computer. Each curve was derived as follows: First, values of $-X$ to $+X$ are provided by the time-ramp integrator 01. This function is squared by a quarter square multiplier (QSM), amplifier 02. The antilog of this exponent, the gaussian function, is then generated by introducing the X^2 function into log amplifier 03. Recorder tracings corresponding to X, $X^2/10$, $-Ae^{-X^2/10C}$ (amplifier outputs 01, 02, 03, respectively) are shown in Fig. 2. The straight-line segments visible in the normal frequency-distribution curve can be either eliminated by filtering or reduced by using a high-accuracy multiplier. This filtering is done by a parallel resistor-capacitor network in the feedback loop of amplifier 04, whose output is also shown in Fig. 2. To complete the program, amplifier 05 integrates the distribution function.

Location of peaks is controlled by the operation of amplifiers 06, 07, 08, and 12 and their associated network (Fig. 1). Their operation is as follows: The output of the summing amplifier 06 (curve 06, Fig. 2) is held positive until amplifier 07 (curve 07) is triggered

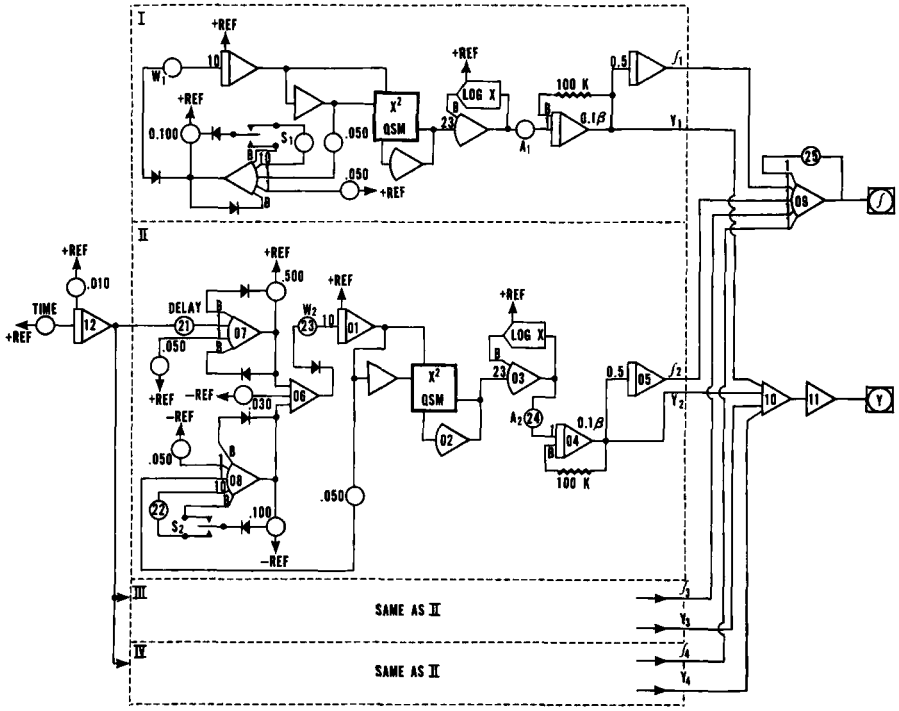

FIG. 1. Analog-computer program for the resolution of four overlapping distributions: *W*, width control; *A*, amplitude control; *S*, skewing control. All diodes are IN 459.

by the time ramp of amplifier 12 through potentiometer 21, which delays the action of the circuit for any desired time. Once amplifier 06 has a negative output, the diode between it and amplifier 01 conducts and the necessary time ramp from $-X$ to $+X$ is produced at the output of amplifier 01. Amplifier 08 (curve 08) limits the output voltage of amplifier 01 by making the output of amplifier 06 positive, which cuts off the diode and stops amplifier 01 from integrating. Amplifiers 07 and 08 thus produce a square-wave output at amplifier 06, as shown, which is integrated by amplifier 01 to give the necessary $-X$ to $+X$ time ramp. Since the first curve is started with the computer, it needs no triggering circuit.

Width of the gaussian curve is a function of the slope of the X curve vs. time and is controlled by potentiometer 23. The amplitude of the curve is simply determined by the output of voltage divider 24.

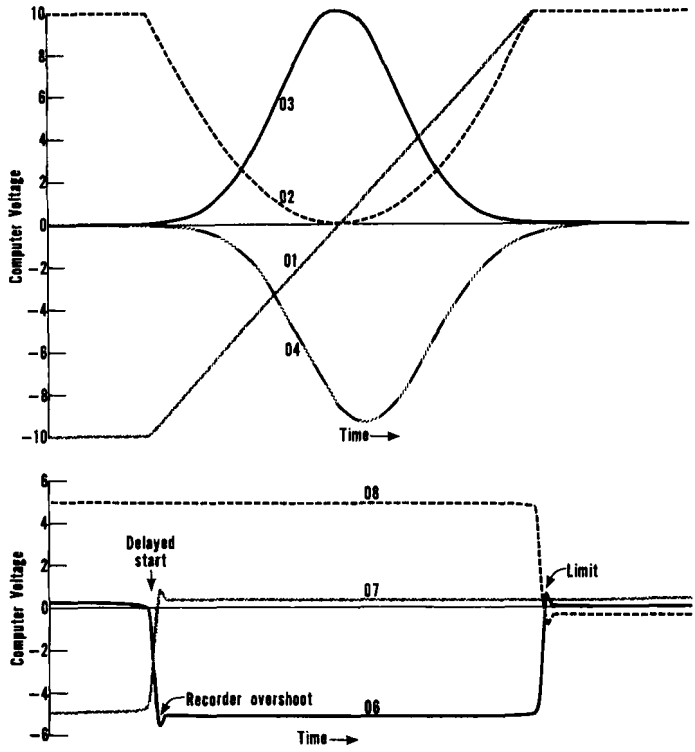

FIG. 2. Recorder tracings of analog functions generated and voltages of switching circuits. Numbers refer to amplifier outputs for program shown in Fig. 1.

Provision is made for varying the positive skewing of curves by switching in a potentiometer in one arm of the diode circuit of the amplifier 08. Inserting the potentiometer generates a saw-tooth output at amplifier 06 which, when integrated, gives a concavely bowed function that substitutes for the linear X. Thus adjustment of potentiometer 22 determines the degree of skewing.

To simulate "stair-step" integral curves, such as are given by various integrator outputs for chromatography, nuclear magnetic resonance, and the like, the areas under the four curves are summed by amplifier 09, whose output is scaled by potentiometer 25 to prevent overload and to permit various sensitivities in the experimental integral curves to be matched. Amplifier 10 has as its input the Y functions of all four gaussian-curve generators. Thus amplifier

11 produces the summation curve of the four distributions, which is compared to the experimental data to be matched.

This circuit is as readily applicable to repetitive operation as it is to plotting on an XY recorder. When used in a repetitive-operation mode and with a multichannel oscilloscope, any combination of or all of the distributions, summation, and integral curves can be observed simultaneously.

RESULTS

Resolution of the four overlapping curves from the countercurrent distribution of the glycerides of cocoa butter is illustrated in Fig. 3 (3). Calculation of the component curves had previously been

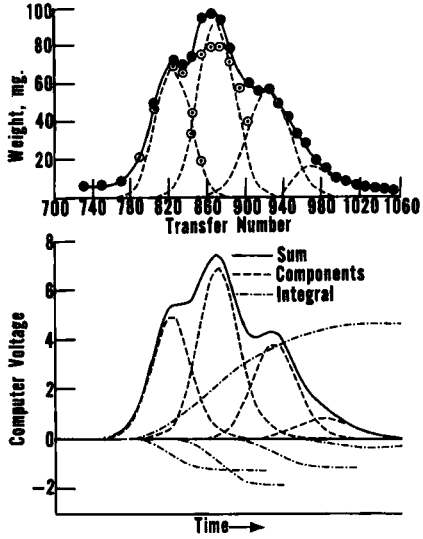

FIG. 3. Countercurrent distribution for the glycerides of cocoa butter resolved by arithmetic and computer calculations.

feasible by the use of the following equation, which relates the ratio of solvent-layer volumes R, partition coefficient K, the number of transfer stages n, the abscissa X, and the ordinate Y:

$$Y = \frac{1}{(2\pi n/RK)^{-1/2}} e^{-X^2/(2n/RK)}$$

As guided by chemical analytical points, the involved mathematical

TABLE 1
Analysis of Cocoa Butter Triglycerides (%)[a]

	SOS	POS	POP	L
Analog	27.6	40.1	24.9	7.3
Calculated	26.1	38.1	26.5	8.4

[a] SOS, distearoolein; POS, palmitostearoolein; POP, dipalmitoolein, palmitodiolein, and triolein; and L, linolein.

procedure of calculating and summing of the component curves and comparing the sum with experimental data was reduced, but, even so, matching constituted a major arithmetic undertaking.

By using an analog computer, the experimental data of Fig. 3 were first approximated by visual matching on a four-channel oscilloscope. For the more precise final stages, the slower, but more accurate, process of using an *XY* recorder was employed. The integrals of area under the individual component curves are shown as the curves with negative ordinates, and the sum of four integrals is shown as the transversing positive curve. The percentage composition for each of the individual triglyceride components is then merely the ratio of the integral of individual components to that of the summed integral.

A comparison of the analyses of cocoa butter triglycerides is shown in Table 1 for the published calculated approximation of the weight curve (3) and for the analog simulation of Fig. 3.

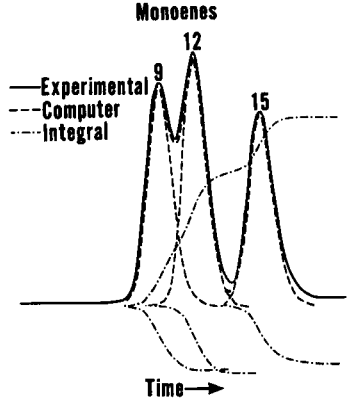

FIG. 4. Matching of capillary gas-chromatographic data showing the separation of a 9-, 12-, and 15-octadecenoate mixtures.

TABLE 2
Analysis of a 9-, 12-, and 15-Octadecenoate Mixture (%)

	9	12	15
Analog	34.3	35.5	30.3
Planimetric[a]	35.6	34.9	29.5
Dibasic acids[b]	36.2	33.5	29.5

[a] The planimetric procedure uses the sharp front side of the 9-octadecenoate distribution as a "template" for the front sides of the 12- and 15-octadecenoate distributions.

[b] The dibasic acid analysis was performed after oxidative cleavage of the monoenes.

The utility of this analog-computer procedure for resolving capillary gas-chromatographic curves is illustrated in Fig. 4. The three peaks displayed correspond from left to right to 9-, 12-, and 15-octadecenoate (5). Whereas the third is quite well resolved, estimation of the overlap of the first two esters would be considerably uncertain by conventional methods of triangulation or by similar approximations. The three integral curves corresponding to the area under the three component curves are shown, as well as the summation of the integrals.

Comparison of methods for analyzing this monoene mixture is illustrated in Table 2.

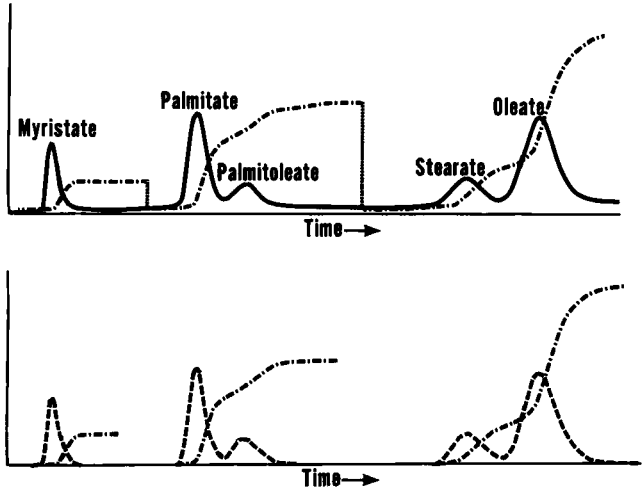

FIG. 5. Simulation of skewed curves on a packed gas-chromatographic column (top) of poor resolution and by a computer (bottom).

Efficacy of the skewing capability is illustrated in Fig. 5. This gas-chromatographic separation of the National Institutes of Health (NIH) Standard Mixture D was purposely chosen for its poor resolution. Marked positive skewing is shown for the myristate peak, but it is adequately simulated by proper adjustment of the skewing potentiometer. The resolution of the two pairs of overlapping skewed curves is also illustrated for the remaining four peaks.

Listed in Table 3 are analytical values for the NIH Mixture D as

TABLE 3
Analysis of NIH Mixture D[a]

	M	P	Pol	S	O
Weighed	11.8	23.6	6.9	13.1	44.6
Integrator of the gas-liquid chromatograph	9.5	23.1	10.1	11.8	45.5
Analog	10.3	24.2	12.1	12.4	42.4

[a] M, myristate; P, palmitate; Pol, palmitoleate; S, stearate; and O, oleate. National Institutes of Health Standard.

weighed, analyzed with an argon ionization detector chromatograph and integrator system (data illustrated in Fig. 5), and as simulated and integrated on the analog computer.

DISCUSSION

An advantage of the rigorous generation of the gaussian functions on an analog computer over other electrical curve-fitting techniques is that the settings of the potentiometers adjusted during curve-fitting operations are related directly to parameters of the function and that the values of these settings may be determined precisely. If smoothing by filtering the output of the log-function generator is omitted, the value of potentiometer 23 is inversely related to the standard deviation of the normal form of the gaussian. Further, the mean of the normal form is determined by the gate setting at potentiometer 21 and by potentiometer 23, the relation being derivable from the X scaling potentiometers. In treating data where the percentage is plotted, potentiometer 24 has a derivable relation to the setting of 23. When the parameters of the gaussian functions are related as in countercurrent distribution, for example, in the cocoa

butter studies (Table 1), the resulting doublecheck improves the precision of estimation considerably, speeds the curve-fitting operations, discloses small deviations from theory, and aids in analyzing system performance.

In fitting other types of data in which the mean and standard deviation are independent, it is still relatively easy to adjust potentiometer 21 first and then work back and forth between it and potentiometers 23 and 24 to achieve a good fit. The parameters of the normal curve may then be easily calculated from the settings.

Although the type of skewing used is also analytic, it leads to forms too complicated to be of more than practical interest at present. Also, if symmetrical curves alone are sufficient to the problem, either filtering, as suggested, or gains, other than those specified, may be used.

This computer program is not limited to the applications presented here to illustrate its versatility. The program should also be useful in a variety of situations where components of summed distribution functions must be determined.

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