

An Improved System for the Conductometric Determination of Hop Alpha-Acids¹

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ABSTRACT

An integrated analytical procedure and calculation approach was developed for the conductometric determination of α -acids in hops. A digital conductivity meter was designed and constructed for following the titration. A programmable printing calculator was used to perform the calculations and to provide a written record of the titration. This analysis system is capable of handling both direct linear conductivity results from a conductance bridge circuit and data obtained with the digital meter (using the appropriate transformations). Results obtained with this method are very similar in magnitude and more precise than results obtained with the conventional procedure. This system also offers improvement in documentation and error detection and is faster and more convenient to use.

Key words: *Digital conductivity meter, Lead acetate titration, Linear regression, Numerical method, Programmable calculator, Transformation*

Conductometric titration with lead acetate is a widely used standard method for the measurement of α -acids in hops and hop preparations (1,3,4). Although some laboratories where large numbers of hop samples are analyzed use instruments that automatically plot the titration curve, many brewery laboratories determine the conductivity after each of a number of incremental additions of titrant. The conductivity measurement is made with a conductance bridge circuit or with a more expensive direct reading conductivity meter. To obtain a single conductivity measurement with one of the conventional conductivity bridge circuits, either a meter or an electric eye tube must be balanced, and the adjusting dial position is then noted. This is time-consuming and, with the electric eye tube, somewhat inaccurate. A circuit described by F. L. Rigby (5) provides an inexpensive direct meter indication that is faster and more convenient to use than a conductance bridge. A modification of this circuit to provide a digital display is described here, along with an integrated computational procedure that calculates and displays the α -acids content of the hops by a nongraphical method.

EXPERIMENTAL

Extraction of Hops

Hops were ground and extracted as described in ASBC Method HOPS-6 using toluene (1).

Standardization

The standardization was done as described in HOPS-6,B.

Titration

The lead acetate titrant was added in uniform 300- μ l increments with a 0-0.5 ml Dispensette (Brinkmann Instruments) instead of a burette. After each addition of titrant, the conductivity was measured with either a conductivity bridge, model RC 1682 (Beckman Instruments) or with a digital conductivity meter designed and assembled in our laboratory (Fig. 1). This is essentially the circuit described by F. L. Rigby (5) extended to include a digital voltmeter as the display device.

Computation

A computational approach was taken for calculating the slopes and intercepts of the two converging lines by linear regression analysis. The intercept point was then computed, and this defined the end point of the titration.

A program for a programmable calculator (Texas Instruments TI-59 with PC-100A printer) has been developed to perform this calculation. The alphanumeric capability of the calculator is used to label the various inputs and outputs. The program is written so that the titration increment (in milliliters) and end point of the standardization are entered and used to arrive at the correction factor (Fig. 2). The weight and moisture content for each sample are entered, followed by the conductance values measured initially and after each increment of titrant. After the last entry, the calculator finds the inflection point; discards a few points nearest the inflection point; and calculates the slope, intercept, and correlation coefficient for each line. (The latter is printed to permit evaluation of the titration accuracy.) The intercept point is computed and the corresponding α -acids content is printed, both "as is" and as corrected for moisture. The conductivity values initially entered are then plotted by the calculator to permit visual evaluation of the titration. A flow chart containing the steps of the calculator program is shown in Fig. 3.²

RESULTS AND DISCUSSION

In principle, the procedure described here does not differ from the standard ASBC conductometric titration method. A digital instrument such as this one eliminates some of the problems associated with analog meters, such as improper interpolation and parallax error. This unit was built of high quality components at minimal cost.

Constant volume additions of titrant can easily and accurately be made with a repetitive pipetting device. This simplifies the analysis both in performing the linear regression and in plotting the data.

Linear regression analysis permits the use of nearly all the data points in arriving at the result; this helps to minimize the error caused by random experimental variation. The calculator program is stored on a magnetic card and loaded into the calculator when it is needed, providing a tested computational procedure. All entries are neatly recorded and can be verified by examining the tape. Incorrectly keyed-in values are readily detected by examining the correlation coefficients and the plot provided.

An evaluation of results obtained with the digital conductivity instrument showed that the lines bowed outward on both sides at higher conductivity values (Fig. 4), which did not happen with results obtained on the same sample with a bridge conductivity instrument. This was puzzling at first, but a careful analysis of the circuit showed why this result was obtained.

The circuit used for measurement can be simplified conceptually to that in Fig. 5A. This is actually an AC circuit, but since the measurement is only done during half of the AC wave (because of the diode) we can treat it as if it were a DC circuit. The circuit can even be simplified conceptually to the point that a resistor network R_N is substituted for the effect of the balancing resistor R_B and the measurement resistor R_M (Fig. 5B).

The property we desire to measure is the solution conductivity, C . This is inversely related to the resistance of the solution, R_s :

²A program listing will be provided by the author upon request.

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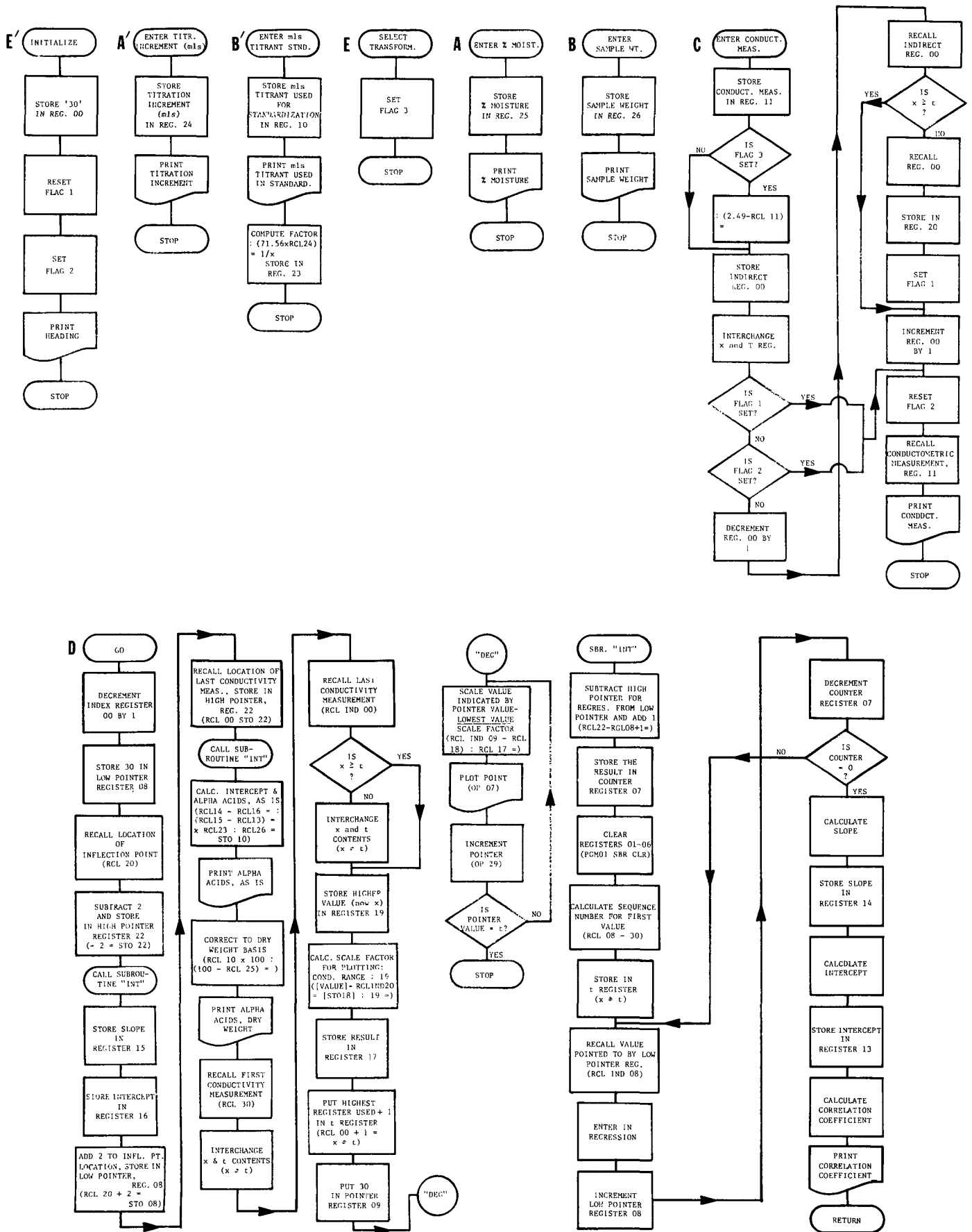


Fig. 3. Conductometric titration calculator program flowchart.

This can be substituted in equation 6 as:

$$C = \frac{\frac{e_T}{R_T}}{e_T - e_N} = \frac{e_T}{R_T(e_T - e_N)} \quad (9)$$

Substituting equation 7 in equation 9 yields:

$$C = \frac{e_T}{(R_S + R_N)(e_T - e_N)}$$

where $R_S = 1/C$:

$$C = \frac{e_T}{(1/C + R_N)(e_T - e_N)}$$

This can be rearranged to:

$$C = \frac{e_N}{R_N(e_T - e_N)} \quad (10)$$

The measured voltage, e_M , is a defined fraction of the resistor network voltage, e_N :

$$e_M = ke_N, \text{ or } e_N = \frac{e_M}{k}$$

Substituting this in equation 10:

$$C = \frac{\frac{e_M}{k}}{R_N\left(e_T - \frac{e_M}{k}\right)}$$

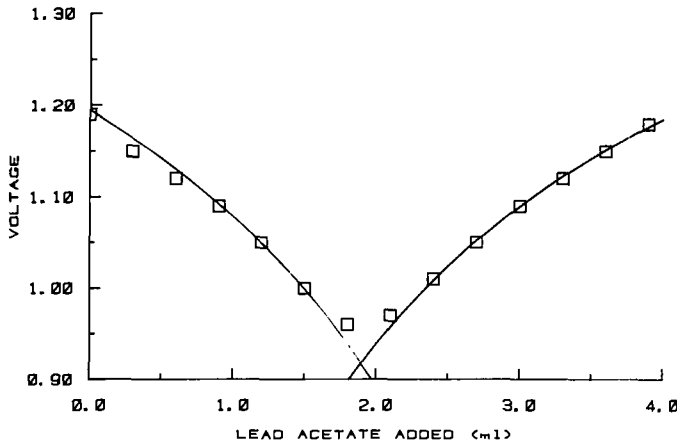


Fig. 4. Titration of α -acids with digital conductivity meter.

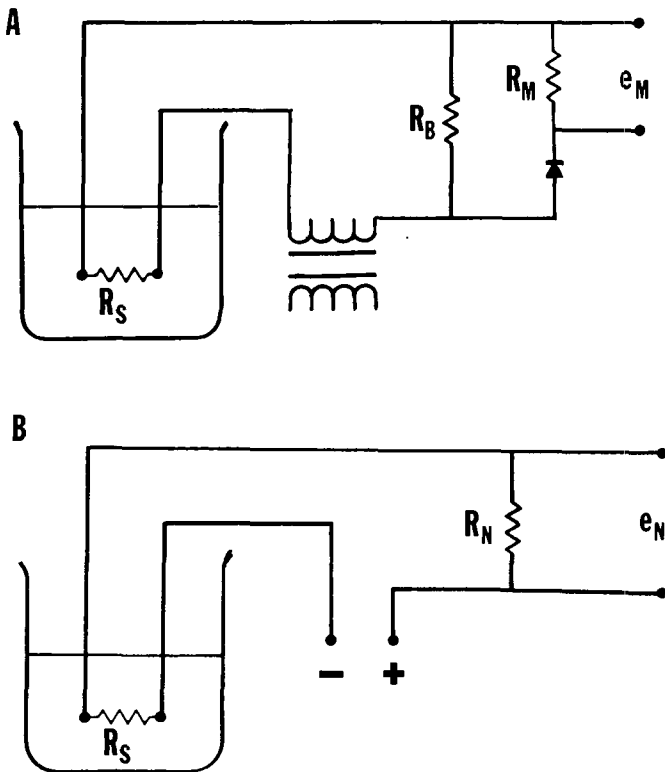


Fig. 5. A, Simplified schematic of digital conductivity instrument; B, direct current analog of the simplified circuit. R_S = resistance of the solution, R_B = balancing resistor, R_M = measurement resistor, e_M = voltage across the measurement resistor, R_N = resistor network, e_N = voltage across the network.

TABLE I
Titrations of Aliquots of the Same Samples
with Bridge Circuit and Digital Meter

	Sample							
	1		2		3		4	
Titrant (ml)	Cond. ^a	/Volt. ^b	Cond.	Volt.	Cond.	Volt.	Cond.	Volt.
0	56.0	1.43	52.0	1.38	47.0	1.33	47.0	1.33
0.3	52.0	1.39	48.0	1.33	43.0	1.28	43.0	1.28
0.6	49.0	1.35	44.5	1.29	39.5	1.22	39.0	1.22
0.9	46.0	1.32	40.5	1.24	35.5	1.15	35.0	1.15
1.2	43.0	1.25	37.0	1.17	31.5	1.08	31.7	1.08
1.5	39.5	1.20	33.5	1.11	34.5	1.12	34.0	1.13
1.8	35.5	1.14	33.0	1.09	38.5	1.19	38.5	1.20
2.1	35.0	1.13	36.0	1.14	42.5	1.26	42.0	1.27
2.4	38.0	1.18	40.0	1.20	46.5	1.32	47.0	1.33
2.7	41.0	1.23	43.2	1.24
3.0	44.5	1.28	46.0	1.30
3.3	48.5	1.32	50.5	1.35
3.6	52.0	1.36
3.9	55.5	1.40

^aConductivity measured with bridge circuit.

^bVoltage measured with digital meter.

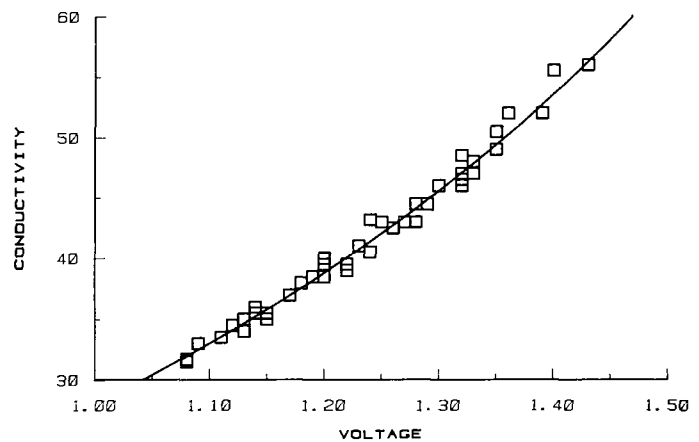


Fig. 6. Plot of conductivity versus voltage for data of Table I.

and rearranging yields:

$$C = \frac{e_M}{R_N(k e_T - e_M)} \tag{11}$$

where R_N , k , and e_T are fixed in any given set of measurements. This means that C is proportional to:

$$\frac{e_M}{k' - e_M} \tag{12}$$

where k' is some complex constant. This relationship holds for any similar circuit, such as that described by Rigby (5), and indicates that the measured voltage is not linearly related to the conductivity. A similar relationship (derivation not shown) applies if current rather than voltage is measured:

C is proportional to $\frac{i_N}{k' - i_N}$.

Because

e_M is proportional to $\frac{C}{k' - e_M}$,

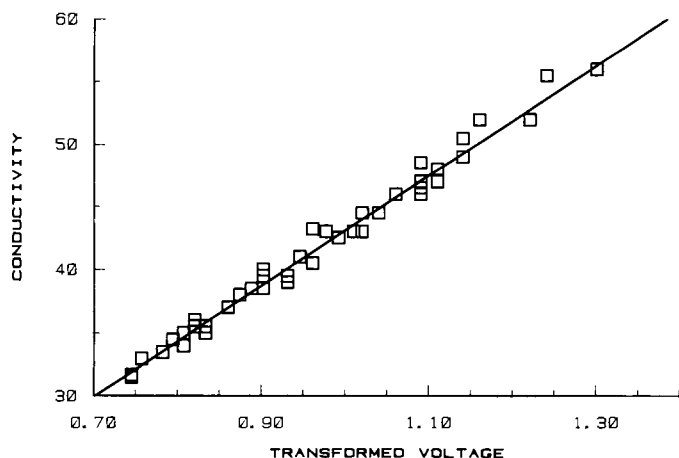


Fig. 7. Plot of conductivity versus voltage, transformed by $e_M / (2.49 - e_M)$ for data of Table I.

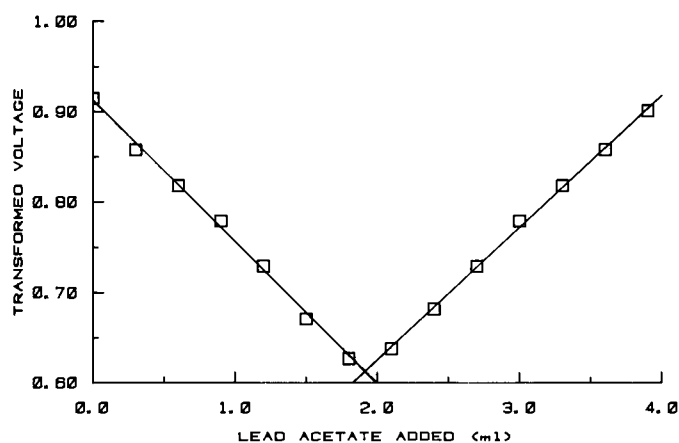


Fig. 8. Titration of α -acids with digital conductivity meter. Data of Fig. 4; voltage results transformed by $e_M / (2.49 - e_M)$.

the measured voltage is nearly linear with conductivity only where e_M is quite small in relation to k' . At higher conductivity (and higher voltage) this relationship diverges significantly from linearity as seen in Fig. 4. Mathematical correction of results is possible, however.

For a particular set of operating conditions (given values of e_T and settings of the potentiometers), a number can be found that will linearize the conductivity measurements. Four sets of comparisons were made in which one aliquot of a toluene extract of a hop sample was titrated using a conductivity bridge and a second aliquot of the same sample was titrated using the digital meter. The conductivity and voltage results are shown in Table I. These results were supplied to a curve-fitting computer program. In all four cases, the best fitting formula, as evidenced by the highest index of determination, was for a hyperbolic function of the type:

$$C = \frac{e_M}{A - B \cdot e_M}$$

The curve-fitting program was then used to calculate the best fit formula through the data points from all four comparisons (Fig. 6):

$$C = \frac{e_M}{0.0596 - 0.0239 \cdot e_M}$$

This can be rearranged to:

$$C = \frac{e_M}{0.0239(2.49 - e_M)}$$

TABLE II
Comparison of Results (dry weight) for α -Acids
Obtained with Aliquots of the Same Sample

Sample	Titrated with		
	Conductivity Bridge	Digital Meter	
		Not Transformed	Transformed
1	8.87	8.51	8.53
2	7.08	7.50	7.51
3	5.37	5.67	5.61
4	5.28	5.56	5.53
5	6.48	6.59	6.44
6	6.02	6.00	5.98

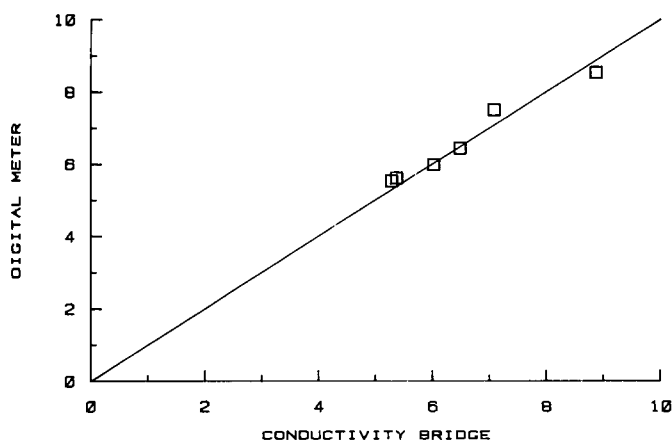


Fig. 9. Comparison of results obtained with paired aliquots of six samples: conductance bridge conductivity result versus digital meter result transformed by $e_M / (2.49 - e_M)$.

TABLE III
Duplicate α -Acids Determinations with Conductivity Bridge^a

Sample	α -Acids (% dry weight)		Mean α -Acids	d^2
1	8.02	7.84	7.93	0.0324
2	8.34	8.45	8.40	0.0121
3	8.69	8.17	8.43	0.2704
4	8.51	8.12	8.32	0.1521
5	8.60	8.47	8.54	0.0169
6	8.37	8.88	8.63	0.2601
7	9.35	8.84	9.10	0.2601
8	8.70	9.22	8.96	0.2704
9	8.48	8.65	8.57	0.0289
10	8.10	7.16	7.63	0.8836
Total			84.51	2.187
Mean			8.45	

$$^a \text{Pooled variance} = S^2 = \frac{\sum d_i^2}{2 \cdot g} = \frac{2.187}{2(10)} = 0.1094$$

where d is the difference between duplicate observations and g is the number of sets of observations.

$$S = \sqrt{S^2} = \sqrt{0.1094} = 0.331$$

$$\text{Pooled coefficient of variation} = \frac{0.331}{8.45} \times 100 = 3.92.$$

This equation is of exactly the same type as equation 12, indicating that the results agree with the electronic analysis. The voltage results in Table I were transformed by $e_M / (2.49 - e_M)$ and plotted versus the observed conductivity (Fig. 7). Excellent agreement with a linear relationship was observed.

The voltage results shown in Fig. 4 were transformed by the same equation and plotted in Fig. 8. A considerable improvement in linearity was obtained. The curvature previously noted at higher conductivities disappeared.

The calculator program was modified to permit transformation of each data point by the indicated formula. The program can thus be used on results from instruments that respond linearly with conductivity (such as a conductivity bridge) by omitting the transformation option, and it can be used to linearize data from instruments that respond nonlinearly (such as the digital meter) by selecting the transformation option. The correct number to be used in the transformation is dependent on the operating parameters of the measuring instrument. In practice, if the settings, once established, are not changed, the same transformation can always be used with that instrument.

A comparison was made of the two approaches. Separate hop samples were extracted; from each extract one aliquot was taken and titrated with a conventional conductivity bridge. The results were calculated by inspection of the points and separate calculation of the two line formulas and intersection points. A second aliquot was taken from each extract and titrated with the digital meter. These results were supplied to the calculator program both with and without the use of transformation. Table II summarizes the findings. Very good agreement was obtained between the two titrations in each case (Fig. 9); the line drawn here is not fit to the data but rather depicts the condition for perfect agreement between the two sets of results. The experimental points are in good agreement with this line, indicating that the two approaches give very comparable results. The difference in results caused by transformation is fairly small, at least in this limited sample.

The precision of the methods was evaluated by comparing results obtained with 10 hop samples determined in duplicate with the bridge conductivity instrument and the previous calculation procedure (Table III) and 10 hop samples determined in duplicate with the digital instrument and the calculator program using the

TABLE IV
Duplicate α -Acids Determinations with Digital Conductivity Meter and Calculation with Calculator Program (Using Transformation)^a

Sample	α -Acids (% dry weight)		Mean α -Acids	d^2
1	7.22	7.45	7.34	0.0529
2	8.80	8.54	8.67	0.0676
3	7.51	7.53	7.52	0.0004
4	7.82	7.69	7.76	0.0169
5	7.26	7.05	7.16	0.0441
6	8.36	7.99	8.18	0.1369
7	7.80	7.62	7.71	0.0324
8	7.09	7.32	7.21	0.0529
9	7.12	6.90	7.01	0.0484
10	7.81	7.86	7.84	0.0025
Total			76.40	0.4550
Mean			7.64	

$$^a \text{Pooled variance} = S^2 = \frac{\sum d_i^2}{2 \cdot g} = \frac{0.4550}{2(10)} = 0.0228$$

where d is the difference between duplicate observations and g is the number of sets of observations.

$$S = \sqrt{S^2} = \sqrt{0.0228} = 0.154$$

$$\text{Pooled coefficient of variation} = \frac{0.154}{7.64} \times 100 = 2.02.$$

transformation (Table IV). In each case, a calculation of pooled variance was made by the formula:

$$S^2 = \frac{\sum d_i^2}{2 \cdot g}$$

where d_i is the difference between the two replicates in a pair of observations and g is the number of observation pairs (2). From the pooled variance, the pooled standard deviation can be found and the coefficient of variation calculated. The two sets of data compare one entire analytical procedure—extraction, titration, and calculation—with the other. With the use of the digital titrator and the calculator program, the coefficient of variation was reduced to 2.02 from the 3.92 of the previous approach. The ratio of the variances is 4.80, and an f -test indicates a 95% probability that the variance obtained with the digital titrator system is less than the variance obtained with the other method.

The digital measurement apparatus described here has been in continuous use for over two years and has been found to be significantly faster, more convenient, and more reproducible than the use of the conductance bridge. The calculator program has been in use for about one year and it, too, has resulted in considerable time savings over the previous method.

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