

# Digital filters in the evaluation of titration curves

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The shape of a titration curve contains useful information, which may be extracted in terms of orthogonal polynomial coefficients. In this way, it is possible to (i) distinguish a monobasic acid from a polybasic acid, having groups of closely similar strength; (ii) detect acid-base impurities in acids and bases, and (iii) study medium effects. The choice of polynomial, range, number of points and experimental conditions are discussed. Using twelve point polynomials and equipment of modest performance, the  $P_1$  coefficient (for the central half of a monobasic acid titration curve) can be measured with a relative standard deviation of 0.58.

Instrumental methods have led to a substantial increase in the quantity of numerical data, which may be ascertained for a given sample. Whereas a pair of numbers (e.g. the volume of acid required to neutralize a given volume of sample) emerges from each gravimetric or volumetric assay, a mathematical *function* (e.g. a graph of pH against volume) may emerge from an instrumental method, like potentiometric titration. Furthermore, when extracting a maximum of chemical information, a function necessarily requires more complicated arithmetic than does a pair of numbers. Hence, when dealing with a function, the use of simple arithmetic, entirely adequate to gravimetric or volumetric results, will normally lead to much loss of information. Such a loss is bound to occur, in fact, if the analyst selects a maximum or minimum value from an instrumental curve and ignores all other values, when calculating the result. This loss is wholly concerned with the shape of the function and so certain principles of curve fitting (Draper & Smith, 1966) are bound to play an important role in any attempt to increase the yield of information. Nevertheless, we must emphasize that, *despite the use of curve fitting arithmetic, the present work is not concerned with curve fitting in the usual sense.*

## PRINCIPLES OF CURVE FITTING

### (a) *Summation of curves*

In Fig. 1a,  $f(v)$  is a function of the abscissa variable,  $v$ , and is reproduced by summing the three functions in Fig. 1b. Thus, for a given abscissa value,  $v_k$ , we can write:

$$f(v_k) = A_0(v_k) + A_1(v_k) + A_2(v_k) \quad \dots \quad \dots \quad \dots \quad (1)$$

This means that the value,  $f(v_k)$ , in Fig. 1a is obtained by taking a sum of the values ( $A_0(v_k)$ ,  $A_1(v_k)$  and  $A_2(v_k)$ ), read from the three curves in Fig. 1b (all these ordinate values referring to the same abscissa value,  $v_k$ ). By repeating this process at many points on the abscissa, we could construct the entire curve,  $f(v)$ , by summing

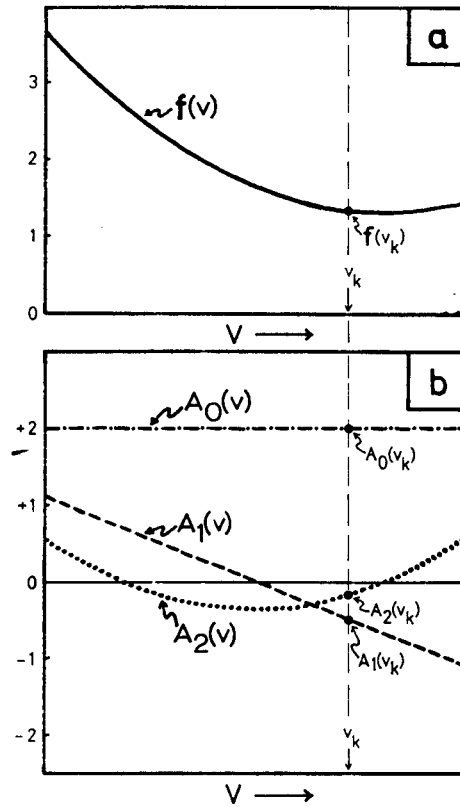


FIG. 1. Summation of component curves.

the three curves ( $A_0(v)$ ,  $A_1(v)$  and  $A_2(v)$ ) in Fig. 1b. Hence, in more general terms, equation (1) becomes

$$f(v) = A_0(v) + A_1(v) + A_2(v) \quad \dots \quad \dots \quad (2)$$

where  $A_0(v)$ ,  $A_1(v)$  and  $A_2(v)$  are *mathematical components* of the function,  $f(v)$ , and equation (2) is a mathematical *model* thereof.

These mathematical components evidently determine the shape of the curve  $f(v)$ . Thus, if  $A_2(v)$  were absent,  $f(v)$  would become a straight line. In a similar way, the overall slope of  $f(v)$  depends upon the component,  $A_1(v)$ . Moreover, we can claim to have *fitted* the curve,  $f(v)$ , as soon as its mathematical components have been calculated by the method detailed below and tested for statistical significance, where necessary.

(b) *Standard mathematical components*

The above exercise would be trivial if the mathematical components were arbitrary and so curve fitting always proceeds on a basis of particular mathematical functions, which in the present context, may be regarded as no more than a set of standard shapes. For most experimental purposes, orthogonal polynomials (Fig. 2) afford the most useful set (Milne, 1949; Davies, 1958; Buckingham, 1962).

The curves in Fig. 2 were constructed from tables of orthogonal polynomials (Fisher & Yates, 1957). These give ordinate values of the polynomial at a specified

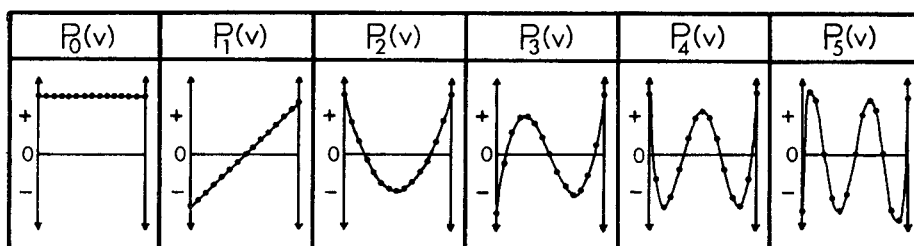


FIG. 2. Orthogonal polynomials. In each diagram,  $P_1(v)$  is plotted against a set of *equally spaced* abscissa values,  $v_0, v_1, v_2, \dots, v_n$ , the same set being used in all six diagrams. Each set of points represents a fundamental curve shape, whose general characteristics are indicated by the line which joins them.

number of points, equally spaced on a generalized abscissa scale (“ $v$ ” in this paper); for example, one such table gives  $P_1(v)$  for 12 equally spaced values of  $v$ . For any given polynomial, the number of points varies from table to table and, in the present case, Fig. 2 was constructed from “15 point polynomials”.

We can now reveal that the three curves in Fig. 1b were obtained by using coefficients ( $p_0, p_1$  and  $p_2$ ) to adjust the scale of the curves,  $P_0(v), P_1(v)$  and  $P_2(v)$ , in Fig. 2. Thus,

$$A_0(v) = p_0P_0(v), \quad A_1(v) = p_1P_1(v) \quad \text{and} \quad A_2(v) = p_2P_2(v)$$

so that

$$f(v) = p_0P_0(v) + p_1P_1(v) + p_2P_2(v) \quad \dots \quad \dots \quad (3)$$

The shape of  $f(v)$  is thus determined by the magnitudes of coefficients  $p_0, p_1$  and  $p_2$ : if  $f(v)$  were more curved,  $p_2$  would be greater, whilst if it possessed no overall slope,  $p_1$  would be zero.

(c) Calculation of coefficients

Calculation of the mathematical components of  $f(v)$  is greatly simplified by the use of polynomials, which are orthogonal. Thus, to obtain coefficients of 12 point polynomials for the curve in Fig. 1a, it is only necessary to:

- (i) note the ordinate values of  $f(v)$  at 12 *equally spaced* points on the abscissa ( $v$ ).
- (ii) multiply each ordinate value by the appropriate integer in the Table of orthogonal polynomials (Fisher & Yates, 1957, see Table 1) (the first ordinate value times the first integer in the Table, the second ordinate value times the second integer in the Table, and so on).
- (iii) sum the products obtained in (ii) and then divide by the normalizing factor, given at the bottom of the Table (and in brackets in Table 1).

Such a calculation is set out in Table 1, wherein the data (used to plot Fig. 1a) appears in the first two columns, 12 point polynomials in the next four columns and the necessary products in the last four columns.

Each product is obtained by multiplying the value of  $f(v)$  in the same row by the appropriate value of the polynomial, also in the same row. For example, in the first row, the product,  $-40.15$ , is equal to  $3.65 \times (-11)$ .

In clarifying the arithmetic, Table 1 gives a false impression of the real arithmetical labour. An electric desk calculator, which is suitable for statistical work, sums the products automatically, whilst with a desk top computer, values of the orthogonal polynomials can often form part of the program, in which case, it is only necessary

for the operator to insert the correct program and enter the values of  $f(v)$  in numerical order.

Table 1. Calculation of orthogonal polynomial coefficients.

Data		Orthogonal Polynomials				Products			
v	f(v)	P <sub>0</sub> (v)	P <sub>1</sub> (v)	P <sub>2</sub> (v)	P <sub>3</sub> (v)	f(v)P <sub>0</sub> (v)	f(v)P <sub>1</sub> (v)	f(v)P <sub>2</sub> (v)	f(v)P <sub>3</sub> (v)
0.25	3.65	+1	-11	+55	-33	+3.65	-40.15	+200.75	-120.45
0.50	3.15	+1	-9	+25	+3	+3.15	-28.35	+78.75	+9.45
0.75	2.71	+1	-7	+1	+21	+2.71	-18.97	+2.71	+56.91
1.00	2.33	+1	-5	-17	+25	+2.33	-11.65	-39.61	+58.25
1.25	2.01	+1	-3	-29	+19	+2.01	-6.03	-58.29	+38.19
1.50	1.75	+1	-1	-35	+7	+1.75	-1.75	-61.25	+12.25
1.75	1.55	+1	+1	-35	-7	+1.55	+1.55	-54.25	-10.85
2.00	1.41	+1	+3	-29	-19	+1.41	+4.23	-40.89	-26.79
2.25	1.33	+1	+5	-17	-25	+1.33	+6.65	-22.61	-33.25
2.50	1.31	+1	+7	+1	-21	+1.31	+9.17	+1.31	-27.51
2.75	1.35	+1	+9	+25	-3	+1.35	+12.15	+33.75	-4.05
3.00	1.45	+1	+11	+55	+33	+1.45	+15.95	+79.75	+47.85
		(12)	(572)	(12,012)	(5148)				
Sums of products		..	..	..	..	+24.00	-57.20	+120.12	0.00
Orthogonal polynomial coefficients		..	..	..	..	2.00	-0.10	+0.01	0.00

From the coefficients at the bottom of Table 1, the curve in Fig. 1a evidently contains constant (P<sub>0</sub>), linear (P<sub>1</sub>) and quadratic (P<sub>2</sub>) components but no cubic (P<sub>3</sub>) component.

The values of  $f(v)$ , used to plot the curve in Fig. 1a and provide data for Table 1, were deliberately chosen to obtain an exact fit from equation (3). Thus, on substituting the above coefficients, equation (3) becomes

for  $v = 0.25$ ,

$$[(2.00) \times (+1)] + [(-0.10) \times (-11)] + [(+0.01) \times (+55)] = 3.65 = f(0.25)$$

for  $v = 0.50$ ,

$$[(2.00) \times (+1)] + [(-0.10) \times (-9)] + [(+0.01) \times (+25)] = 3.15 = f(0.50)$$

for  $v = 0.75$ ,

$$[(2.00) \times (+1)] + [(-0.10) \times (-7)] + [(+0.01) \times (+1)] = 2.71 = f(0.75)$$

For each abscissa point, these expressions calculate the values of  $A_0(v)$ ,  $A_1(v)$  and  $A_2(v)$  in Fig. 1b and sum them to obtain the corresponding value of  $f(v)$  in Fig. 1a. Such an exact fit is most unlikely to occur in practice and, if  $f(v)$  were derived from experiment, observational errors would almost certainly lead to a non-zero value of  $p_3$ . Hence, some coefficients are devoid of statistical significance (Davies, 1958).

(d) *Simplicity of calculation*

From the above example, it is evident that, if measurements are equally spaced on the abscissa scale, it is very easy to specify the shape of an experimental curve by calculating one or more orthogonal polynomial coefficients. In other words, it is very easy to extract most of the information, contained in an experimental function.

DIGITAL FILTERING

With increased availability of computers, the need to extract more information from instrumental techniques has been increasingly recognized (Fenwick, 1932; Gran,

1952; Feates & Ives, 1956; Sternberg, Stillo & others, 1960; Jones, Seshadri & others, 1963; Katakis, 1965; Fraser & Suzuki, 1966; Wernimont, 1967; Westerberg, 1969; Anderson, Gibb & Littlewood, 1970).

The present paper follows earlier work (Glenn, 1963; Glenn, 1967; Agwu & Glenn, 1967) in using a technique, more recently known as *digital filtering* (Blackburn, 1969) which is no more than a computer analogue of the communication engineer's well known technique of electrical filtering. In digital filtering, electrical filters are replaced by the arithmetic of curve fitting, but, as we shall argue below, digital filters should not be restricted to the usual objectives of curve fitting, for in the hands of communications engineers, electrical filters have been used with greater imagination!

*The aim of filtering, whether electrical or digital, is to reject some part of the experimental function and so obtain a more reliable and useful conclusion.* A pertinent analogy would concern a communications engineer asked to measure the intensity of sound emitted by a whistle, when blown at a busy traffic junction during the rush hour. In these circumstances, a huge positive error would emerge from a straightforward measurement of the gross intensity of sound and so special apparatus would be essential.

Fig. 3 shows the kind of apparatus, which would be suitable for a whistle, having a fundamental of 4KHz. The microphone and amplifier convert the total sound input to a measurable electrical signal, having a complicated waveform (A). This signal then passes through a 4KHz filter, when all frequencies which lie outside the passband of the filter are absorbed and only a small range of frequencies (B) are allowed to reach the A.C. meter. After suitable calibration, the latter would give a greatly improved estimate of the desired sound intensity.

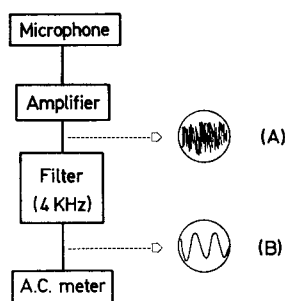


FIG. 3. Isolation of a signal from a noisy background.

The ability of the filter to reject unwanted sound is inversely related to the width of its passband; that is, assuming average conditions, wherein the unwanted sound is well distributed throughout the frequency range, 0–15 KHz (serious error might, however, result from a small boy with a similar whistle!).

The characteristic sound of a whistle resides more in its harmonics than in its fundamental frequency. Hence, if the filtered signal were applied to a loudspeaker instead of the A.C. meter, a somewhat characterless note would emerge. Nevertheless, the use of additional filters (at 8KHz, 12KHz and 16KHz) to measure the intensity of these harmonics (and so extract the full character of the whistle) would multiply the risk of interference from unwanted sound. In other words, additional filters would merely provide additional channels, through which the unwanted sound

could affect the meter. On average, it is unwise to use more than one channel in this kind of application.

The above example demonstrates two points:

(1) For some purposes, an experimental function can be adequately represented by only one of its mathematical components. This applies to the above example, in which the whistle was adequately represented by its 4KHz component. It also applies to the present work, wherein the central half of a titration curve is represented by just one component, other statistically significant components being unnecessary.

(2) For some purposes, it may be very unwise to represent an experimental function by *more than* one of its mathematical components. This applies to problems of background interference, as in the above example and also in spectrophotometric analysis (Wright, 1941; Glenn, 1963). Nevertheless, although relevant to the general problem of digital filtering, this point does not apply to the present analysis of titration curves, wherein the use of one component is a matter of convenience rather than necessity.

These two points justify an earlier statement, namely that, despite the use of curve fitting arithmetic, *the present work is not concerned with curve fitting in the usual sense.*

Curve fitting is usually concerned with *faithful models* of experimental functions and is mainly directed towards the elimination of observational error. Such an approach is equivalent to a communications engineer's use of a low pass filter to remove high frequency electrical noise, which often represents a high proportion of the total error of observation. Nevertheless, electrical filters can be used in other ways (p. 185S) and the same is also true of digital filters (or curve fitting arithmetic).

As in earlier work, this paper is concerned with useful *working models* of experimental functions and, in deriving such models, a number of statistically significant mathematical components are usually omitted. In consequence, one of our working models may differ very greatly from the corresponding faithful model, but this may be turned to advantage in some cases (p. 185S) and may constitute no material disadvantage in others.

In spectrophotometric analysis, the well known "base-line" method (Mulder, Spruit & Keuning, 1963) is an apt example of digital filtering, even as a purely graphical operation. It extracts the quadratic ( $P_2$ ) component and rejects the constant ( $P_0$ ) and linear ( $P_1$ ) components of the absorption curve. For assay purposes, the quadratic component is a good working model of the compound's absorption curve.

#### *Information obtainable from the shape of a titration curve*

It is common practice to ignore the shape of a titration curve and confine attention to one or two abscissa points, such as the equivalence point and pH at half neutralisation, in the case of a monobasic acid. Although the shapes of small segments of a titration curve are important to the evaluation of equivalence points by derivative methods, the latter can hardly be said to evaluate shape in the present context.

By evaluating the shape of a titration curve, or a substantial segment thereof, we take account of more data than hitherto and, therefore expect an improvement, either in the quality or quantity of information produced. This is certainly true of a derivative method, which takes account of an appreciable segment of the curve (Fenwick, 1932). Moreover, in the authors' experience, the accuracy of a poorly defined equivalence point is greatly improved when the derivative is obtained by a

convolution process (Savitzky & Golay, 1964), which spans a reasonably large segment of the curve.

The scope of potentiometric titration is currently limited by the fact that even Savitzky & Golay's approach has difficulty in detecting an equivalence point between two stages of neutralization, which are associated with a difference of less than 2 units in  $pK_a$ . Nevertheless, from results obtained in the present work, evaluation of orthogonal polynomial coefficients would seem to offer good prospects for tackling this kind of difficulty in cases where the two stages can be separately characterized. Thus, even in the case of a mixture of two monobasic acids, which differ by as little as 0.5 unit in  $pK_a$ , the  $P_1$  coefficient is still fairly sensitive to the composition of the mixture.

By evaluating  $p_1$  for a substantial segment, it is relatively easy to distinguish between the curve of a monobasic acid and a curve which relates to a mixture of monobasic acids or to the overlapping stages of a polybasic acid. Such an approach may, therefore, be useful to investigations of molecular structure, where knowledge of the number of individual acid-base groups in a molecule is not only valuable in its own right, but is also essential to the calculation of a molecular weight from a titration curve. The same approach may also prove useful to the quality control of acid-base solutions, particularly in view of results obtained in the present work.

For quantifying solvent effects, acid-base interactions and association (King, 1965), there is much to be said for the use of orthogonal polynomial coefficients, based upon a substantial segment of the curve. In this respect, an accurate potentiometric titration constitutes a rapid method for detecting and quantifying the non-ideal behaviour of an acid-base system (see p. 192S).

When using a given polynomial (e.g.  $P_1$ ) to quantify such effects,

$$p_1(\text{effect}) = p_1(\text{observed}) - p_1(\text{theoretical})$$

where  $p_1(\text{effect})$  is a measure of non-ideal behaviour and  $p_1(\text{theoretical})$  is obtained by substituting species concentrations into the appropriate acid-base equation (Ricci, 1952) and then calculating  $p_1$ , as in Table 2.

The present paper is concerned with an initial study of the potentialities of orthogonal polynomials in evaluating titration curves. To this end, it is essential,

Table 2. *Theoretical values of  $p_1 \times 10^5$  for monobasic acids. [0.25–0.75 neutralization; 12 point polynomial ( $n = 11$ )]*

$pK_a$	1.0 molar	0.1 molar
1 (or 13)	3222.6	2316.6
2 (or 12)	4010.7	3222.6
3 (or 11)	4190.2	4010.7
4 (or 10)	4211.2	4190.2
5 (or 9)	4213.4	4211.2
6 (or 8)	4213.6	4213.4
7	4213.8	4213.6

Values of  $p_1 \times 10^5$  in Table 2 were based on pH's calculated from the following expression:

$$[H^+] = K_a \left( \frac{c(1-x)-y}{xc+y} \right) \text{ where } x \text{ is the fraction of neutralization,}$$

and  $c$ , the stoichiometric molarity of acid. For  $pK_a \leq 6$ ,  $y = [H^+]$  and for  $pK_a \geq 8$ ,  $y = -[OH^-]$ . For  $pK_a = 7$ ,  $y = 0$ .

Deviation of the  $pK_a$  from 7 and reduction of concentration both produce a decrease in the magnitude of  $p_1$ .

not only to choose a suitable function, range of application and number of points, but also, to estimate the order of accuracy with which chosen coefficients can be measured by normal chemical procedures.

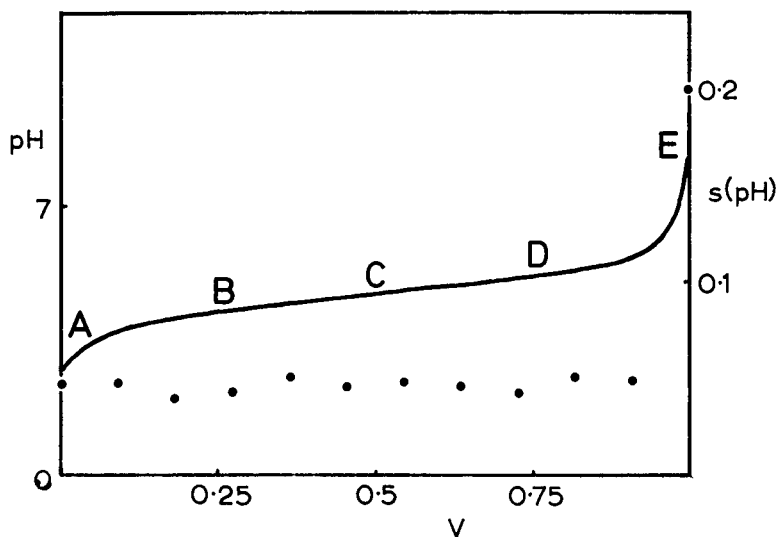


FIG. 4. Monobasic acid titration curve: standard deviation of pH measurement at different fractions of neutralization. ● =  $s(\text{pH})$ .

#### *Choice of function and range*

The typical weak monobasic acid curve of Fig. 4 provides a useful basis for the choice of function and range. Bearing in mind the principles outlined on p. 182S, the entire curve, A—E, can be seen to originate mainly from the mathematical components,  $P_0(v)$ ,  $P_1(v)$  and  $P_3(v)$ . Moreover, in view of the relation between the shape of a monobasic acid curve and the  $\text{pK}$  of the acid, it is evident that coefficients,  $p_0$  and  $p_3$ , are highly dependent upon  $\text{pK}$ ,  $p_0$  bearing a substantially linear relationship thereto, whilst  $p_3$  is a more or less linear function of  $|\text{pK} - \text{pH}(\text{neutrality})|$ . Apart from such high dependence upon  $\text{pK}$ , there is an added disadvantage that the poorly buffered regions, AB and DE, must inevitably provide major contributions to the error of the calculated coefficients. Similar objections apply to regions, AB, AC, CE and DE, but not to the region, BD, which therefore represents a good choice for most purposes. The further decision to assign B to 25% and D to 75% neutralization throughout the present work reflects a desire for the safety of a well buffered region.

Between 25 and 75% neutralization,  $p_0$  and  $p_1$  are the only significant coefficients. Moreover, the usefulness of  $p_0$  in the study of solvent effects is underlined by the fact that  $\Delta p_0 = \Delta \text{pK}$  for small values of  $\Delta \text{pK}$ .

#### *The number of points*

This part of the discussion refers to a general form of equation (3), namely,

$$f(v) = p_0P_0(v) + p_1P_1(v) + p_2P_2(v) + \dots + p_nP_n(v) \quad \dots \quad (4)$$

Perfect representation of a *continuous* experimental function, such as a titration curve, may demand an infinite number of terms in equation (4), in which case, one would



need to measure  $f(v)$  at infinitesimal intervals of  $v$ . In practice, however, one can never do more than sample the continuous function at a discrete set of abscissa values. Thus, in view of restrictions, such as the limits of reading a chart or the inevitable truncation of a digital output, all experimental variables are granular.

The effect of taking too small a sample is evident from the simple example in Fig. 5, wherein two different continuous functions,  $f_1(v)$  and  $f_2(v)$  give identical values of a given coefficient for the set,  $(v = 1, 3, 5)$ , but two different values of the same coefficient for the set,  $(v = 1, 2, 3, 4, 5)$ . In other words,  $f_1(v)$  and  $f_2(v)$  are indistinguishable when sampled at  $v = 1, 3$  and  $5$ , this phenomenon being known as "aliasing" (Blackburn, 1969).

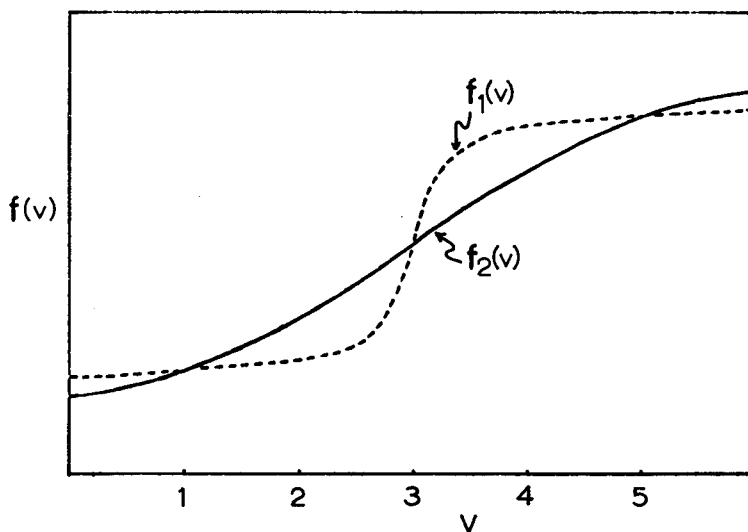


FIG. 5. The number of points.

Sudden fluctuations in  $f(v)$ , arising from features such as a spike, hump (or step in the case of a titration curve), contribute to the coefficients of higher terms in equation (4). Moreover, the number of terms in (4) is limited to the number of points,  $(n + 1)$  and so  $n$  must always exceed the order of the highest term, which is statistically significant ( $n$  should, in fact, exceed this lower limit by a comfortable margin, in view of the tendency for observational errors to move from lower to higher terms as  $n$  increases). Hence, in determining the coefficients of lower polynomials, an adequate number of points is often a good deal larger than the bare minimum required to calculate the coefficient in question (e.g. 2 points for  $p_1$ ).

In comparing coefficients obtained from equivalent segments of different titration curves, it is essential to adhere to a constant number of points. The latter must, therefore, be chosen in the light of that curve which contains the largest fluctuation in  $f(v)$  within the segment analysed.

An increase in the number of points also affects the reproducibility of the observed coefficients and in view of special circumstances, may be shown to reduce the relative standard deviation of the  $P_1$  coefficient, used throughout the present work.

Substituting pH for  $f(v)$  and using  $s(x)$  to denote the estimated standard deviation of quantity,  $x$ ,  $s(p_1)$  is approximately equal (Davies, 1958) to  $s(\text{pH})/N_1^{\frac{1}{2}}$ , where  $N_1$

is the normalizing factor for  $P_1(v)$ ; that is, 572 for 12 points.  $s(\text{pH})$  refers to the observational error of pH measurement, which to validate the expression for  $s(p_1)$ , must be homogeneous over the set of points used to calculate  $p_1$ . Nevertheless, apart from small regions at the start and finish of a monobasic acid titration curve, there should be no difficulty in achieving reasonable homogeneity of  $s(\text{pH})$ , which can only depend upon errors in the measurement of pH and  $v$  respectively. Of these two contributions, the one due to pH measurement should be constant for measurements in aqueous solvents which avoid extremes of pH, whilst that due to  $v$  should also be constant if the curve undergoes no great variation in slope over the segment analysed. From the results in Fig. 4, the anticipated good homogeneity of  $s(\text{pH})$  was evidently achieved over most of the curve for acetic acid,  $s(\text{pH})$  at the equivalence point being the sole exception.

The present work involved analysis of an approximately linear segment of titration curve, spanning about 1 pH, and in these circumstances,

$$p_1 \approx \frac{\sum_{i=0}^{i=n} (i/n)P_1(v_i)/N_1}{\sum_{i=0}^{i=n} (i/n)P_1(v_i)} \text{ so that } r.s.(p_1) \approx \frac{100 s(\text{pH}) N_1^\dagger}{\sum_{i=0}^{i=n} (i/n)P_1(v_i)} \quad \dots \quad (5)$$

where  $i = 0, 1, 2, \dots, n$  and r.s. denotes relative standard deviation (or coefficient of variation, which term might confuse the reader in present circumstances).

Theoretical values of  $r.s.(p_1)$ , obtained by substituting the convenient value,  $s(\text{pH}) = 0.01$ , into the last formula, are shown in Fig. 6. There is evidently a useful reduction in  $r.s.(p_1)$  to be gained by increasing  $n$ , over and above the bare minimum,  $n = 1$ .

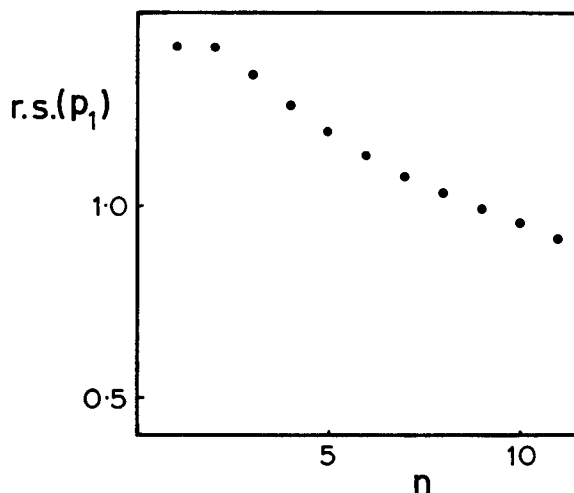


FIG. 6. Relative standard deviation of  $p_1$  and the number of points.

#### *Instrumentation and technique*

The preliminary investigation now reported was carried through with a pH meter of modest performance and with no more than the usual technique for producing titration curves, accurate by present day standards. In consequence, it was only by extensive replication that the smaller differences between mean coefficients in Table 3

achieved significance. Improved instrumentation and technique on the other hand might well have reduced the number of replicates required to discriminate a given difference.

The accuracy and precision of coefficients depends not only upon operator technique but also upon maintenance of a linear pH/e.m.f. relationship of constant slope. Furthermore, although electrode standardization must remain constant throughout the measurement of a given coefficient, its accuracy is unimportant to the determination of any coefficient other than  $p_0$ . With a slide wire linearity of 0.01% and ability to discriminate  $\pm 0.0005$  pH, a modern pH meter will achieve these requirements to within  $\pm 0.0005$  pH over a range of 1 pH unit, particularly when equipped with a single helical potentiometer which eliminates switch contact potentials from the slide wire system. In these circumstances, attainment of the desired pH/e.m.f. characteristics is effectively determined by the electrode system.

Under the dynamic conditions of an ordinary potentiometric titration, deficiencies of the electrode system mainly arise from hysteresis (Beck, Caudle & others, 1963) of the glass electrode and from the temperature coefficients of both electrodes. Some glass electrodes require a long time to reach the pH of the surrounding solution and in a titration of reasonable duration, the observed pH may lag behind the true value by as much as 0.05 pH. Moreover, the isothermal condition so necessary to meaningful pH measurement is destroyed by the heat of neutralization, which can raise the temperature by  $1^\circ$  in the course of titration, so affecting the pH/e.m.f. relationship as well as the potentials of reference electrode and inner half-cell of the glass electrode. The slope of the pH/e.m.f. relationship also depends upon other factors such as the electromotive efficiency (British Standards, 1965) of the glass electrode and the efficiency of the guard ring (Parker, 1950) both of which may fluctuate from day to day.

The last factors can be remedied by calibration, which for the limited purpose of quality control may also reduce the adverse effects of glass electrode hysteresis and thermal shifts. For this purpose, bracketing a given titration by titrations of a pure reference acid would seem to offer a powerful though laborious calibration procedure. For other purposes however, such as the study of solvent effects, it would seem advisable to (i) allow adequate time for electrode equilibration; (ii) stabilize both temperature and ionic strength and (iii) control factors such as electromotive efficiency by calibration with two buffers.

Using a free piston burette, titrant volume can be controlled to a limit (e.g. 0.01 ml in 20 ml) equivalent to about 0.0005 pH over the range of neutralization employed in the present work. Titrant volumes can be made integral by taking a suitable weight of titrand, based on a prior titration to complete neutralization. Coulometric generation of titrant would however be more attractive in view of the possibility of automating the process in conjunction with a pH meter giving a digital print out.

### *Experimental procedures*

Organic acids were lab. grade, except for acetic acid (Analytical Reagent). In all titrations, 0.5M NaOH aq., contained in a Jencon free piston burette, was added to 40 milliequivalents of acid in 100 ml of water. Titrant volumes necessary to produce 12 readings, equally spaced on the abscissa scale, between 0.25 and 0.75 of total neutralization, were calculated from a prior titration. pHs were measured on a Cambridge Bench Type pH meter (discrimination: approximately 0.01 pH) using

glass (General Purpose) (British Standard, 1965) and saturated calomel electrodes, the temperature compensator being set to lab. temperature ( $19.6 \pm 2^\circ$ ). Each titration was completed in about 30 min during which time the reading on M/20 potassium hydrogen phthalate drifted by less than 0.02 pH, usually toward higher values. The electromotive efficiency of the glass electrode, checked with phthalate and borate buffers at 2 hourly intervals, was never less than 0.996.

#### Discussion of results

In Table 3, each block (except *c*) refers to a set of replicate titrations of a given sample of acid, carried through in the course of two or three days. Trends between blocks were probably reduced, but not eliminated, by the use of the same glass electrode throughout all blocks. In block *c*, two samples of propionic acid were titrated alternately, in order to minimize the effect of trends.

Table 3. *Titration of mono- and di-carboxylic acids: mean values of orthogonal polynomial coefficients (0.25–0.75 neutralization;  $n = 11$ ) and relative standard deviations thereof.*

Block	Acid	pK <sub>a</sub> (25°C)	Mean value of coefficient $\times 10^5$ , relative standard deviation, degrees of freedom	
			p <sub>1</sub>	p <sub>3</sub>
<i>a</i>	Acetic	4.76	4219, 0.59%, 9 (0.00%)	—
<i>b</i>	Propionic	4.88	4136, 0.61%, 9 (-1.97%)	—
<i>c</i>	Propionic	Fraction I	4125, 0.59%, 9 (-2.23%)	—
		Fraction V	4084, 0.83%, 9 (-3.20%)	—
<i>d</i>	Acetic Propionic	4.76 4.88	0.12 } 4162, 1.46%, 8 (-1.35%)	—
<i>e</i>	Oxalic	1.23	2.96 } 11 090, 0.49%, 9 (+163%)	-399, 0.92%, 9
		4.19		
<i>f</i>	Malonic	2.84	2.86 } 12 700, 0.44%, 9 (+201%)	-502, 1.30%, 9
		5.70		
<i>g</i>	Succinic	4.19	1.29 } 5874, 0.39%, 7 (+39.2%)	19, 21%, 7
		5.48		

The relative standard deviations given in Table 3 for all blocks, other than *d*, relate to variances, which, according to Bartlett's test, form a homogeneous set whose mean corresponds with  $s(p_1) = 24.3 \times 10^{-5}$ . This value is approximately equivalent (p. 189S) to  $s(\text{pH}) = 0.0058$ , which is consistent with the equipment and technique employed.

To assist comparison, the percentage deviation from the mean value of  $p_1$  for block *a* is given beneath each mean value of  $p_1$  in Table 3. Small statistically significant differences between means should be regarded with caution in view of possible trends between blocks. The difference between means ( $t = 10.1$ ) for block *a* and Fraction V of block *c* probably reflects the tendency, in aqueous solution, for acetic acid to dimerize to a smaller extent than propionic acid. Thus, whereas acetic acid gave reasonable agreement between observed and theoretical values (Table 2), propionic acid showed a greater divergence on account of its larger association constant (Nash & Monk, 1957).

Differences between the means for blocks *a*, *b* and *d* are relevant to the distinction of mono- from polybasic acids, the  $pK_a$  difference between acetic and propionic acids being less than the theoretical minimum (0.3) for the difference in  $pK_a$  between consecutive stages of a polybasic acid. The statistical significance ( $t = 2.63$ ,  $\phi = 10$ ) for the small difference between mean values of  $p_1$  for blocks *a* and *d* suggests that in view of the much larger  $\Delta pK_a$  likely to arise between consecutive stages of a polybasic acid, a valid distinction would require rather less than the 12 measurements employed throughout the present work. The absence of a significant difference between the mean values of  $p_1$  for blocks *b* and *d* probably arose from a loss of degrees of freedom which resulted from the unusually large variance associated with block *d*.  $p_1$  for succinic acid, whose titration curve exhibits no noticeable inflexion at the first equivalence point, is distinguishable from  $p_1$  for a monobasic acid on the basis of only one titration. For the same acid,  $p_3$  is too small for precise determination by the equipment and technique of the present work. Oxalic and malonic acids on the other hand exhibit  $P_3$  coefficients large enough for precise determination.

To obtain some indication of the potentialities of orthogonal function coefficients in quality control, a sample of propionic acid was separated into five portions by fractional freezing. The first and fifth fractions gave significantly different ( $t = 3.09$ ) mean values of  $p_1$  in an experimental design from which trends in experimental conditions were virtually eliminated. Moreover, as  $p_1$  for a mixture of two acids of similar  $pK_a$  should be greater than that for either acid alone, the means show the anticipated relationship,  $p_1$  for the first, presumably less pure, fraction being larger than that for the fifth fraction.

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