J. Pharm. Pharmac., 1968, **20**, 836–839 Received June 19, 1968

A note on the evaluation of results from creep tests using a computer

S. S. DAVIS AND B. WARBURTON

The accuracy of line spectrum creep analysis depends ultimately on the accuracy with which the steady state compliance of the system with the longest retardation time can be derived. The presented treatment shows how the maximum theoretical value of the creep compliance may be calculated and describes an iterative method for obtaining the correct value using the least sum of squares.

THE rheological examination of pharmaceutical semisolids by creep testing has been reported by Barry & Shotton (1967) and Warburton & Barry (1968). The method is simple and the results may be expressed in terms of fundamental rheological parameters. However, although the analysis of creep curves can be made graphically the procedure is lengthy and not suited to routine investigations. To overcome this, an automatic data logging system and analysis has been devised.

The apparatus used is that of Warburton & Barry (1968). The signal from a transducer bridge, which is a record of the change of strain with time, is attenuated and passed to both a Kent Chart recorder and a digital voltmeter with associated print out. The printer is triggered every 30 sec so that a record of the creep curve is available in graphical and digital forms the latter being punched onto tape for analysis by computer.

The computer analysis is dealt with in two parts.

(1) CREEP CURVE ANALYSIS

Most of the computer analysis is a straight mathematical interpretation of the graphical analysis of creep curves (Warburton & Barry, 1968). However, there are two steps requiring special consideration (the notation used is that of Warburton & Barry, 1968).

Step 1. *The original creep curve.* The essential part of this analysis is to find where the curve becomes linear. The approximate region for the onset of linearity can be deduced from the graph and the experiment allowed to proceed so that the linear region is greater than 25% of the total curve. The computer makes a linear regression on the last 20% of the points and the equation for the straight line is derived. Starting with the longest time, the strain at each time interval is generated from the regression equation and compared with the actual strain. The point for the onset of linearity is obtained when the difference between the two exceeds the maximum difference due to experimental error. The value of the intercept of the regression line on the strain axis leads to an *approximate* value for J(N), the total creep compliance at equilibrium.

Step 2. *Voigt model analysis.* To derive the parameters of the Voigt models that describe a viscoelastic system, a plot is made of the function ln (J(N) − J(t))/J(N) [abbreviated to ln (Zn)] against time where J(t) is

From the Department of Pharmaceutics, The School of Pharmacy, University of London, London, W.C.1, England.

the total creep compliance at time t. As in step 1 the point where a curve becomes a straight line must be found so that the best straight line can be drawn through the points obtained at longer times. The first method of approach was to assume that the curve was linear over the last 20% of the points and then adopt a procedure similar to that in step 1. However the values of ln (Zn) obtained at longer times are dependent on the accuracy of the data and the value chosen for J(N) so that in many cases the derived regression line is nowhere near the best straight line that can be drawn when the whole of the linear region is considered. The points that lie closest to a straight line are obtained immediately after the point where linearity commences. This region must be found before the regression line is calculated and this can be achieved by the method of second derivatives. Starting with time zero the gradient of the straight line through points 0–4 is calculated, this is repeated with points 1–5 and so on until the whole curve has been followed. The 1st derivatives so obtained are then subjected to the same process to give the second derivative values. For a straight line the second derivative values should be zero. In practice, for the linear region, their values fluctuate from small negative to small positive, so by setting limits the extent of the linear region can be determined. The regression line is then calculated, and by comparing the actual value of ln (Zn) with the calculated values, the point for the onset of linearity, found by the derivative method, can be checked. The analysis then follows directly that of Warburton & Barry (1968). Successive Voigt units may be analysed in a similar manner.

(2) THE CHOICE OF THE VALUE OF J(N)

The accuracy of the whole analysis depends on the best fit value of J(N). This is the equilibrium or steady state value as t approaches infinity and is not readily accessible. With computer facilities the best fit value for J(N) is obtained using an iterative procedure. The maximum theoretical value for J(N) can be found by considering the creep compliances at two times t_1 and t_2 where $t_2 = 2t_1$ and where the creep behaviour is due to the Voigt unit of longest retardation time only. Then for time t_1

$$e^{-t_1/\tau} = \frac{J(N) - J(t_1)}{J(N)} \quad \ldots \quad (1)$$

and for time t_2

$$e^{-t_2/\tau} = \frac{J(N) - J(t_2)}{J(N)} \quad \ldots \quad (2)$$

where τ is the longest retardation time. Dividing (2) by (1)

$$\frac{J(N) - J(t_2)}{J(N) - J(t_1)} = e^{-t_1/\tau} \quad \ldots \quad (3)$$

But

$$e^{-t_1/\tau} = \frac{J(N) - J(t_1)}{J(n)} \quad \ldots \quad (4)$$

(Warburton & Barry, 1968)

where J(n) is the compliance due to the Voigt unit of longest retardation time

$$\therefore J(n) = \frac{[J(N) - J(t_1)]^2}{J(N) - J(t_2)} \qquad (5)$$

J(n) = xJ(N) where x is the antilog of the intercept of the J(N) − J(t)/J(N) versus t plot on the ordinate

$$\therefore J(N)^2 - xJ(N)^2 - 2J(N)J(t_1) + xJ(N)J(t_2) + J(t_1)^2 = 0 \qquad (6)$$

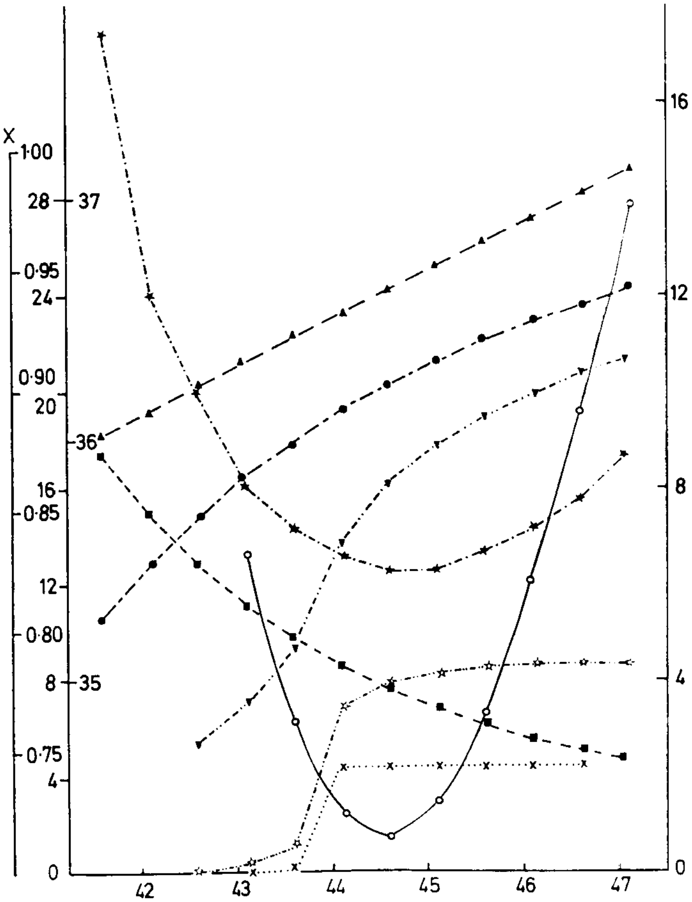

FIG. 1. The effect of the value of J(N) on the viscoelastic parameters of a 3 Voigt Unit System (Emulsifying Ointment B.P.). For notation see Warburton & Barry (1968). —○—, (S); —■—, X; —▲—, τ_2; —▼—, τ_1; —X—, τ_3; —★—, J(n); --●—, J(N) - J(n); —☆—, J(n_3). Ordinates—left hand axes: the 1st represents X; the 2nd represents τ_1, τ_3 (min × 10), which are short and shortest retardation times, and also (S) = sum of squares; the third represents Jn. The right hand axis represents J(n_3), J(N)—J(n), these together with Jn are arbitrary units, one unit being equivalent to a compliance of 1·15 × 10^{-7} cm^2 $dyne^{-1}$. The right hand axis also represents τ_2 (min), which is the longest retardation time.

As the equation is a quadratic, J(N) has a unique and maximum value when '$B^2 - 4AC = 0$'

$$\text{i.e. } x^2J(t_2)^2 - 4J(t_1)xJ(t_2) + 4xJ(t_1)^2 = 0 \qquad (7)$$

i.e. when $x = 0$

$$\text{or } x = \frac{4[J(t_1)\,J(t_2) - J(t_1)^2]}{J(t_2)^2} \qquad (8)$$

$$J(N)_{MAX} = \text{'}-B/2A\text{'}$$

$$\text{i.e.} \qquad J(N)_{MAX} = \frac{2J(t_1) - J(t_2)x}{2(1 - x)} \qquad (9)$$

$J(N)_{MAX}$ can therefore be determined from the derived values of J(t). To find the best fit value of J(N) the approximate value obtained from the linear regression in step 1 is reduced by 10% and then increased progressively to $J(N)_{MAX}$. At each value of J(N) the full creep curve analysis is made and the creep equation for the system is derived. The compliance at each given time interval is then calculated and compared with the experimental values (Barry & Shotton, 1967). The sum of the squares of the differences between the two is calculated (S) and the best fit value of J(N) is obtained where the sum of squares is a minimum.

The effect of the value of J(N) on the derived viscoelastic parameters for a 3 Voigt unit system is shown in Fig. 1. S has a well defined minimum value which can be easily found by this iterative process. It can be seen that the value of J(N) has a profound influence on all the viscoelastic parameters. The best fit value of J(N) is greater than the value found from Step 1 of the creep curve analysis but is less than the maximum value obtained from equation (9).

It is concluded that the use of computer methods will greatly facilitate creep curve analysis and that by using iterative methods accurate values are obtained for viscoelastic parameters.

References

Barry, B. W. & Shotton, E. (1967). *J. Pharm. Pharmac.*, **19**, *Suppl.*, 121S–129S.
Warburton, B. & Barry, B. W. (1968). *Ibid.*, **20**, 255–268.