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ESTIMATION OF DIFFUSIVITY USING S-PLUS

by

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Computer Centre

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1 Introduction

Mathematical models provide one of the basic tools for describing physical processes and for explaining and predicting behaviour under varying conditions. Recently, computers have stimulated greater interest in the mathematical modelling of food science processes involving heat transfer (sterilisation, blanching, freezing) and mass transfer (leaching, blanching, drying, osmotic processing. smoking, &c.) (Daudin, 1983; Karel, 1976; Schwartzberg & Chao, 1982).

Diffusion is a physical process that involves mass transfer. The uptake or loss of solutes from solids is partly controlled by diffusion and is an important component in unit operations. Movement of food additives such as sodium chloride, calcium chloride, sorbic acid, sugars and combinations thereof have been examined (Schwartzberg & Chao, 1982; Liu, 1992; Giannakopoulos & Guilbert, 1986) due to their effects on food quality characteristics (texture, flavour, colour, microbiological qualities, and pH). Garrote *et al.* (1984), Califano & Cavelo (1983), and Tomasula & Kempel (1989) used mathematical models to describe solute loss during blanching of vegetables. Diffusion models were used to describe loss of glucose during blanching of potatoes to achieve control of the concentration of the reducing sugars which play an important rôle in non-enzymatic browning reactions. Loss of vegetable nutrients has also been described (Tomasula & Kozempel, 1989; Kozempel, 1982; Selman *et al.*, 1983).

Mass transfer in foods has traditionally been approximated by models based on Fick's law, which is based on concentration gradients (Crank, 1985). During diffusion, solid and liquid come into contact and transfer occurs from liquid to solid (infusion) or from solid to liquid (leaching), depending on relative concentration of solute (Wang & Sastry, 1993).

The present work describes computer procedures for estimating apparent diffusivity in various unit operations where mass and heat transfer occur so that processes can be optimised from an engineering point of view.

2 Theoretical considerations

Quantitative measurement of the rate at which a diffusion process occurs is usually expressed in terms of diffusivity (also called the 'diffusion coefficient'). Diffusivity is defined as the rate of transfer of the diffusing substance across unit area of a section, divided by the space gradient of the concentration of the section. Thus, if the rate of transfer is F, and C the concentration of diffusate, and if x denotes the space coordinate, then

$$F = -D\frac{dC}{dx} \quad \ldots\ldots\ldots\ldots (1)$$

and Eq (1) is a definition of diffusivity D (Crank, 1975). A general form of Fick's second law which can be used to analyze non-steady state diffusion in a symmetric solid is:

$$\frac{\partial C}{\partial t} = \frac{1}{r^{\nu-1}}\frac{\partial}{\partial r}\left(r^{\nu-1}D\frac{\partial C}{\partial r}\right) \quad \ldots\ldots\ldots\ldots (2)$$

where t is time; v is 1 for an infinite slab, 2 for an infinite cylinder, and 3 for a sphere; and r is the distance measured from the centre of the solid.

Crank (1975) presents solutions for Eq (2). For an infinite slab, Fick's second law can be written as:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (3)$$

For long cylinders, assuming the diffusion to be radial and concentration (C) to be a function of radius (r) and time (t) gives:

$$\frac{\partial C}{\partial t} = \frac{1}{r}\left\{\frac{\partial}{\partial r}\left(rD\frac{\partial C}{\partial r}\right)\right\} \qquad (4)$$

For an element of volume of a sphere in which the diffusion is radial, the diffusion equation takes the form:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \qquad (5)$$

Analytical solutions to these equations for the three geometric shapes slab (sheet), cylinder, and sphere are given by Newman (1931) and Crank (1975). They assume constant diffusivity, no resistance to mass transfer in the medium surrounding the solid and no chemical reaction between the solute and the solid.

For a slab we have

$$f(D_A;t,a) = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{-(2n+1)^2\left(\frac{\pi}{2}\right)^2\frac{D_A t}{a^2}\right\} \qquad (6)$$

For a sphere we have

$$f(D_A;t,a) = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{-n^2\pi^2\frac{D_A t}{a^2}\right\} \qquad (7)$$

For a cylinder of infinite length we have

$$f(D_A;t,a) = 4\sum_{n=1}^{\infty}\frac{1}{j_{0,n}^2}\exp\left\{-j_{0,n}^2\frac{D_A t}{a^2}\right\} \qquad (8)$$

and for a cylinder of finite length we have

$$f(D_A;t,a) = \frac{32}{\pi^2}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\frac{1}{(2m+1)^2}\frac{1}{j_{0,n}^2}\exp\left\{-(2m+1)^2\left(\frac{\pi}{2}\right)^2\frac{D_A t}{a_2^2} - j_{0,n}^2\frac{D_A t}{a_1^2}\right\} \qquad (9)$$

In each case, a least squares estimate of apparent diffusivity, D_A, is made by minimising $\sum\{E - f(D_A;t,\mathbf{a})\}^2$ where $f(D_A;t,\mathbf{a})$ is a solution to Fick's second law and $E = \frac{C - C_\infty}{C_0 - C_\infty}$ is the fraction infused or leached at time t; C is average concentration at time t; C_0 is initial concentration; and C_∞ is concentration at the surface; and a is half-thickness, or radius of the target. In the case of the finite-length cylinder, a_1 is radius and a_2 is length. The $j_{0,n}$ are zeroes of Bessel functions of the first kind and zero order (Abramowitz & Stegun, 1972).

3 S-PLUS functions: codes given in the appendix

3.1 *Calculation of* $f(D_A;t,\mathbf{a})$

fickslab, ficksphere, fickcylf and fickcyli evaluate $f(D_A;t,\mathbf{a})$ on a vector of elapsed times for slab, sphere and finite-length cylinder, and infinite-length cylinders geometries respectively. Sums in the expressions for $f(D_A;t,\mathbf{a})$ are computed using twenty terms.

3.2 *Estimation of the diffusivity*

For a given $\mathbf{a}$, C_0,and C_∞, a least squares estimate of diffusivity is obtained with function fick. The function asks for type of geometry, the characteristic dimension, the cylinder length if finite, and the name of a data file; reads data from a file; calculates E; and uses the S-PLUS function ms to minimise $\sum\{E - f(D_A;t,\mathbf{a})\}^2$. The estimate of D_A, observed and predicted values of E and a graph of these values are produced.

Content of the data file comprises two columns. The first row contains values of C_0,and C_∞. Subsequent rows contain pairs of time and concentration values.

4 Examples

4.1 *Example: slab geometry*

The following results were taken from an experiment involving blanching of carrot slices in $CaCl_2$ solution. Slab geometry was used with a half-thickness, a, of 0.00476 m. The first row of the data file contains values for C_0 and C_∞ of 39.9 and 1202.4 respectively.

Data file

```
39.9    1202.4
900     293.471
1800    363.1182
2700    454.8282
3600    518.518
4500    597.2806
5400    633.842
6300    686.3252
7200    723.5898
```

Output

```
"slab geometry, a= 0.00476"
"D= 8.64128590185322e-10"
"Residual sum of squares= 0.000629244895824058"
"R2= 0.99489829609639"
  Observed Predicted
 0.7818744 0.7909460
 0.7219628 0.7043530
 0.6430725 0.6379098
 0.5882856 0.5819252
 0.5205328 0.5327335
 0.4890822 0.4885710
 0.4439353 0.4484759
 0.4118797 0.4118610
```

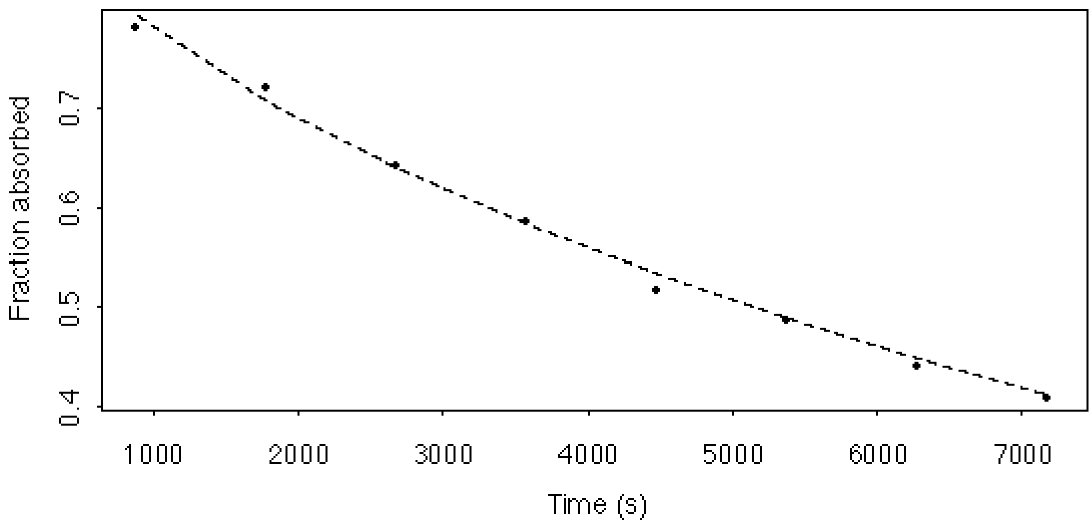

Fig 1. Observed and predicted fraction of calcium absorbed by carrot slices during blanching in 0.3 M $CaCl_2$ solution at 65˚C.

4.2 Example: spherical geometry

The second example involves an investigation of the diffusion of sugar during rehydration of plums (Bocanegra-Miramontes, *et al.*, 1998) under the assumption of zero resistance to mass transfer by the skin. Spherical geometry was used with a radius of 0.016 m.

Data file

```
.34     0.56
0       0.340
1800    0.394
3600    0.417
7200    0.462
9000    0.482
10800   0.500
14400   0.520
21600   0.540
27000   0.542
34200   0.543
41400   0.55
```

Output

```
"sphere geometry, a= 0.016"
"D=  1.6724428715874e-09"
"Residual sum of squares=  0.0293994046111436"
"R2= 0.971310083445499"
  Observed  Predicted
 1.00000000 0.97035089
 0.75454545 0.66819175
 0.65000000 0.55141770
 0.44545455 0.40693968
 0.35454545 0.35556044
 0.27272727 0.31249427
 0.18181818 0.24394567
 0.09090909 0.15158669
 0.08181818 0.10675092
 0.07727273 0.06703700
 0.04545455 0.04212966
```

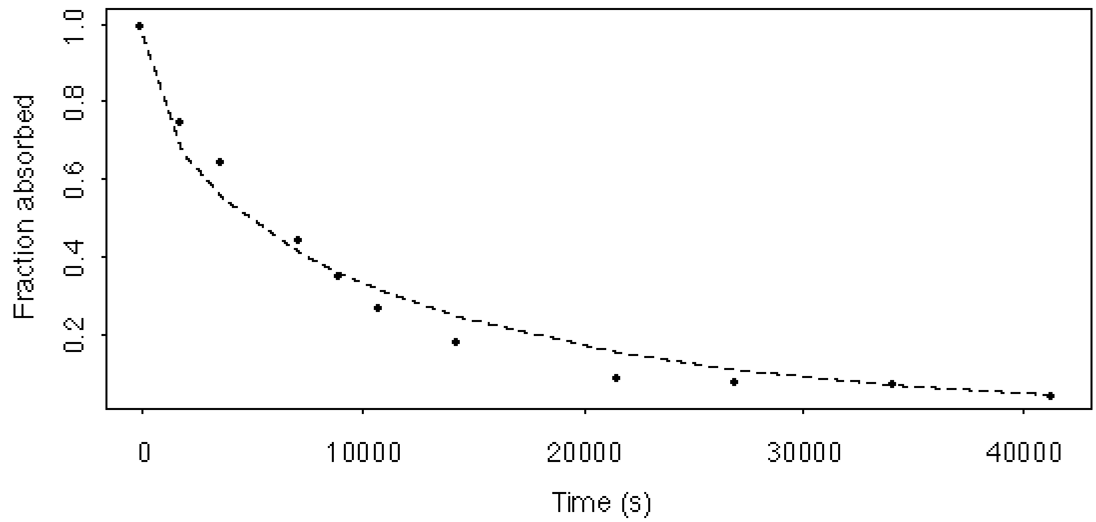

Fig 2. Observed and predicted fraction of sugar absorbed during rehydration of plums in 41˚Bx sugar solution at 22˚C.

4.3 Example: cylindrical geometry, finite length

The third example uses data graphically extracted from results of an experiment on diffusion of NaCl in potato (Liu, 1992). Cylindrical geometry was used with a radius of 0.00625 m and a cylinder length of 0.06 m. Diffusion data for 80˚C and 3% concentration is illustrated.

Data file

```
1.713e+00    28.7
2.257e+02    7.126e+00
4.796e+02    1.018e+01
7.155e+02    1.219e+01
9.503e+02    1.330e+01
1.195e+03    1.546e+01
1.437e+03    1.633e+01
1.673e+03    1.809e+01
1.916e+03    1.871e+01
2.157e+03    1.884e+01
2.425e+03    1.930e+01
2.660e+03    2.106e+01
2.894e+03    2.103e+01
3.145e+03    2.197e+01
3.378e+03    2.227e+01
3.629e+03    2.305e+01
```

Output

```
"calf geometry, a= 0.00625"
"length= 0.06"
"D= 1.98158584795993e-09"
"Residual sum of squares=
0.00596162965064653"
"R2= 0.986313104477137"
  Observed Predicted
 0.7994219 0.7588879
 0.6862563 0.6602282
 0.6117760 0.5940122
 0.5706451 0.5406516
 0.4906066 0.4936475
 0.4583688 0.4533357
 0.3931523 0.4185266
 0.3701782 0.3863899
 0.3653611 0.3575785
 0.3483159 0.3285463
 0.2830993 0.3053288
 0.2842109 0.2840302
 0.2493793 0.2629807
 0.2382629 0.2449367
 0.2093601 0.2269556
```

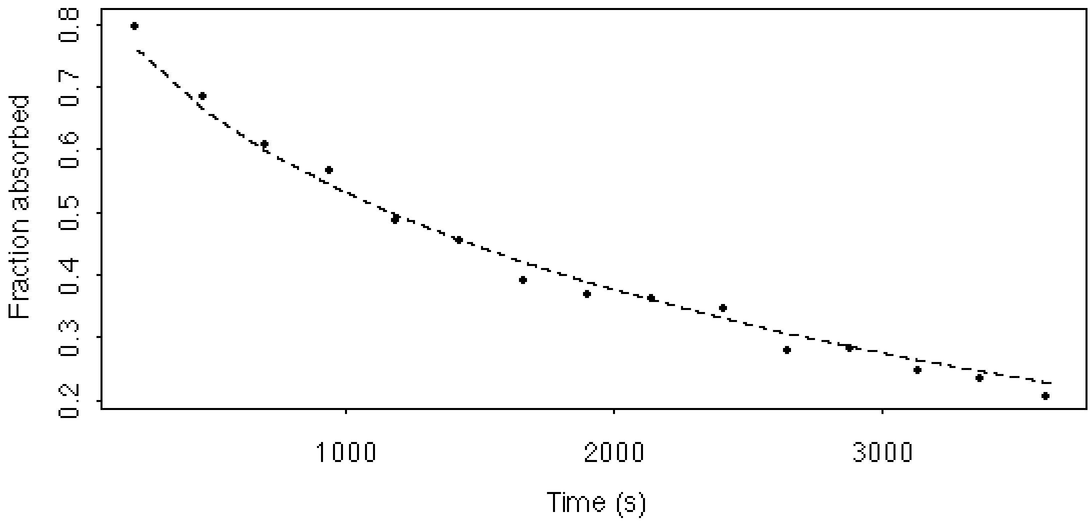

Fig 3. Observed and predicted fraction of NaCl absorbed during infusion of cylinders of potato tissue in 3% NaCl solution at 80˚C under the assumption of finite cylinder length.

4.4 Example: cylindrical geometry, infinite length

The fourth example uses the same data as in the third. Cylindrical geometry was used with a radius of 0.00625 m, this time with the assumption of infinite length.

Data file

```
1.713e+00       28.7
2.257e+02       7.126e+00
4.796e+02       1.018e+01
7.155e+02       1.219e+01
9.503e+02       1.330e+01
1.195e+03       1.546e+01
1.437e+03       1.633e+01
1.673e+03       1.809e+01
1.916e+03       1.871e+01
2.157e+03       1.884e+01
2.425e+03       1.930e+01
2.660e+03       2.106e+01
2.894e+03       2.103e+01
3.145e+03       2.197e+01
3.378e+03       2.227e+01
3.629e+03       2.305e+01
```

Output

```
"cyli geometry, a= 0.00625"
"D= 2.10310967696677e-09"
"Residual sum of squares=
0.00500322241382236"
"R2= 0.988513445740762"
  Observed Predicted
 0.7994219 0.7636650
 0.6862563 0.6640744
 0.6117760 0.5972524
 0.5706451 0.5433118
 0.4906066 0.4956915
 0.4583688 0.4547591
 0.3931523 0.4193439
 0.3701782 0.3865931
 0.3653611 0.3571930
 0.3483159 0.3275405
 0.2830993 0.3038162
 0.2842109 0.2820521
 0.2493793 0.2605499
 0.2382629 0.2421305
 0.2093601 0.2237933
```

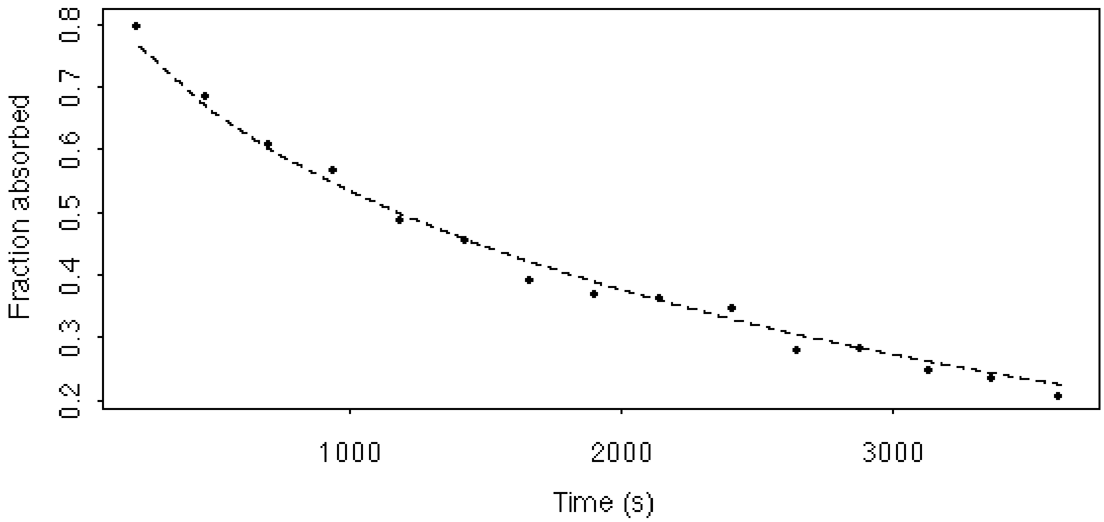

Fig 4. Observed and predicted fraction of NaCl absorbed during infusion of cylinders of potato tissue in 3% NaCl solution at 80˚C under the assumption of infinite cylinder length.

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Selman, J.D., Rice, P. and Abdul-Rezzak, K. (1983) A study of the apparent diffusion coefficients for solute losses from carrot tissue during blanching in water. *Journal of Food Technology*, **18**, 427-440.

Schwartzberg, H.G. & Chao, R.Y. (1982) Solute diffusivities in leaching processes. *Food Technology*, **2**, 73-86.

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APPENDIX

fick

```
#CALCULATE APPARENT DIFFUSIVITY
#Datafile comprises two columns: the value in the first row of the first column
#is initial concentration, the value in the first row of the second column is
#concentration at the surface. Subsequent rows contain time/concentration pairs.
#
#Row 1  c0  ce
#Row 2  t1  c1
#Row 3  t2  c2
#. &c
#Row n  tn  cn
#
fick <- function()
{
  print('Enter geometry -  slab, sphere, cylf, cyli:')
  geom <- readline()
  print('Enter half-thickness/radius:')
  a <- as.numeric(readline())
  if(geom == 'cylf')
  {
    print('Enter length of cyl:')
    b <- as.numeric(readline())
  }
  else b <- NA
  print('Name of datafile:')
  datafile <- readline()
  dat <- read.table(datafile)
  c0 <- dat[[1]][1]
  ce <- dat[[2]][1]
  pos <- 1:length(dat[[1]])
  t <- dat[[1]][pos>1]
  ct <- dat[[2]][pos>1]
  e <- (ct-ce)/(c0-ce)
  dat <- data.frame(t,e)
  parameters(dat) <- list(D=0,a=a,b=b)
  switch(geom,
         slab = mod <- ms( ~ sum((e - fickslab(a,t,D))^2),
                    start=list(D=1e-10), data=dat),
         sphere = mod <- ms( ~ sum((e - ficksphere(a,t,D))^2),
                    start=list(D=1e-10), data=dat),
         cylf = mod <- ms( ~ sum((e - fickcylf(a,b,t,D))^2),
                    start=list(D=1e-10), data=dat),
         cyli = mod <- ms( ~ sum((e - fickcyli(a,t,D))^2),
                    start=list(D=1e-10), data=dat))
#Output
  D <- mod$parameters
  switch(geom,
         slab = ep <- fickslab(a,t,D),
         sphere = ep <- ficksphere(a,t,D),
         cylf = ep <- fickcylf(a,b,t,D),
         cyli = ep <- fickcyli(a,t,D))
  print(paste(geom,'geometry, a=',a))
  if(geom == 'cylf') print(paste('length=',b))
  print(paste('D=',D))
  print(paste('Residual sum of squares=',mod$value))
  print(paste('R2=',1-mod$value/(var(e)*(length(t)-1))))
  y <- matrix(c(e,ep),ncol=2)
  dimnames(y)[2] <- list(c('Observed','Predicted'))
  print(y)
```

```
  #Draw Fick solutions
  if(dev.cur() < 2) motif('-geometry +0+0')
  plot(t, e, type='p', xlab='Time (s)', ylab='Fraction removed')
  lines(t,ep,lty=3)
  title(datafile)
}
```

fickslab, ficksphere, fickcylf and fickcyli

```
#Evaluate predictions for fixed D.
fickslab <- function(a,t,D)
{
  ep <- rep(0, length(t))
  for (n in 0:19)
  {
    ep <- ep + 1/(2*n+1)^2 * exp(-(2*n+1)^2 * pi^2 * (D*t)/(4*a^2))
  }
  ep <- 8/pi^2 * ep
  return( ep )
}

ficksphere <- function(a,t,D)
{
  ep <- rep(0, length(t))
  for (n in 1:20)
  {
    ep <- ep + 1/n^2 * exp(-n^2 * pi^2 * (D*t)/a^2)
  }
  ep <- 6/pi^2 * ep
  return(ep)
}

fickcylf <- function(a1,a2,t,D)
{
  ep <- rep(0, length(t))
  R <- c(2.4048, 5.5201, 8.6537, 11.792, 14.931, 18.071, 21.212, 24.352,
         27,493, 30.635, 33.776, 36.917, 40.058, 43.199, 46,341, 49.482,
         52.624, 55.766, 58.907, 62.048)
  for (n in 1:20)
    for (m in 1:20)
    {
      ep <- ep + 1/(2*m-1)^2 * 1/R[n]^2 *
            exp(-(2*m-1)^2 * (D*t)/a2^2 * (pi/2)^2 - R[n]^2 * (D*t)/a1^2)
    }
  ep <- 32/pi^2 * ep
  return(ep)
}

fickcyli <- function(a,t,D)
{
  ep <- rep(0, length(t))
  R <- c(2.4048, 5.5201, 8.6537, 11.792, 14.931, 18.071, 21.212, 24.352,
         27,493, 30.635, 33.776, 36.917, 40.058, 43.199, 46,341, 49.482,
         52.624, 55.766, 58.907, 62.048)
  for (n in 1:20)
  {
    ep <- ep + 1/R[n]^2 * exp(-R[n]^2 * (D*t)/a^2)
  }
  ep <- 4 * ep
  return(ep)
}
```