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Oxygen Transfer Parameter Estimation

By Michael K. Stenstrom,[1] M. ASCE, Linfield C. Brown,[2] and Hyung J. Hwang[3]

Introduction

Estimating the oxygen transfer rate of an aeration system is one of the more important functions of a process design engineer. Underestimating the oxygen transfer rate of a proposed aeration system results in an overdesigned system which may be energy intensive and expensive to operate. Overestimating the oxygen transfer rate results in inadequate oxygen transfer and reduced process efficiency.

Several methods have been proposed to estimate the oxygen transfer rates of an aeration system, but the most common procedure is to estimate the clean water rate and then translate that rate to field conditions with alpha, beta, and theta correction factor. Estimates of the clean water transfer rate are usually made by determining the volumetric oxygen transfer coefficient and equilibrium oxygen concentration from a nonsteady state reaeration test. Methods and procedures have been described by Bass and Shell (2), Campbell, et al. (7), Schmit, et al. (12), and are also presented in *Standard Methods* (13).

The volumetric mass transfer coefficient and equilibrium dissolved oxygen (DO) concentration are usually estimated by fitting the concentration versus time data to the two-film model, as follows:

$$\frac{dC}{dt} = K_L a(C_\infty^* - C) \quad (1)$$

in which C = DO concentration, in milligrams per liter; C_∞^* = saturation DO

[1] Asst. Prof., Water Resources Program, School of Engrg. and Applied Sci., University of California at Los Angeles, Los Angeles, Calif. 90024.
[2] Assoc. Prof., Dept. of Civ. Engrg., Tufts Univ., Medford, Mass. 02155.
[3] Post-Grad. Research Engr., Water Resources Program, School of Engineering and Applied Science, University of California at Los Angeles, Los Angeles, Calif. 90024.

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concentration, in milligrams per liter, at equilibrium; K_La = volumetric oxygen transfer coefficient, t^{-1}; and t = time.

There are three basic approaches to estimating the parameters K_La and C_∞^* from the data and Eq. 1. One approach is to use the differential method (also called the direct method) by calculating the derivative directly from the data and rearranging Eq. 1 in order to use simple linear regression to estimate K_La and C_∞^*.

The second method, called the log-deficit method, is to integrate Eq. 1 and rearrange the following logarithmic form:

$$\ln|C_\infty^* - C| = -K_La t + \ln|C_\infty^* - C_0| \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

in which C_0 = DO concentration when $t = 0$.

The mass transfer coefficient K_La can be estimated using simple linear regression if C_∞^* is known. Estimates of C_∞^* are often made using handbook values of saturation DO concentration. For submerged aeration systems, the value of C_∞^* is higher than the handbook or surface value of DO, and depth corrections must be made. Also gas-side depletion corrections can be made. This method of estimating C_∞^* is often incorrectly referred to as a model, e.g., the mid-depth corrected model. An alternate approach with the logarithmic technique is to estimate C_∞^* from the data using some type of nonlinear programming technique. A nonlinear programming technique is required because Eq. 2 cannot be made linear in all the parameters, C_∞^*, C_0, and K_La. In the special case where the value of C_∞^* is fitted, the method is called the best-fit log deficit technique.

The third method is to use the exponential, integrated form of Eq. 1, as follows:

$$C = C_\infty^* - (C_\infty^* - C_0)e^{(-K_La\,t)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

To estimate K_La it is necessary to use a nonlinear programming technique, and all three parameters, K_La, C_∞^*, and C_0, are usually estimated.

The advantages and disadvantages of each parameter estimation technique have been reviewed by a number of investigators, including Boyle, Berthouex, and Rooney (5), Campbell, Ball and O'Brien (7), the second writer (1), the first writer (15), and Gilbert and Libby (10). Also a subcommittee of the ASCE Committee on Standards has evaluated parameter estimation techniques. The consensus of all investigators is that the three-parameter exponential form, using some form of nonlinear programming, is the most desirable of all three methods. The best-fit log deficit technique is the second choice.

The advantages that have been determined by previous workers of the exponential nonlinear technique are summarized as follows:

1. Minimizing the sum of squares error for the exponential method minimizes the actual error in oxygen concentration, whereas the logarithmic method minimizes the error of the log of concentration, which is often biased.
2. The residuals (difference between the expected and measured value) are more uniform than other methods. The logarithmic method usually produces larger residuals as C approaches C_∞^*, while the differential method usually produces extremely large residuals for low values of C.
3. Truncation of data as C approaches C_∞^* is not required, as is required in the logarithmic method. High precision of the estimate for C_∞^* is dependent upon having data as C approaches C_∞^*.
4. Since C_∞^* is estimated from the data, no error is introduced by incorrectly estimating C_∞^* from handbook, depth/saturation or correction methods.
5. The precision of the estimates for C_∞^* and K_La is much greater than the precision obtained by the differential method, and usually greater than the precision obtained from the logarithmic method.

The greatest disadvantage of the exponential method is the computational requirements of nonlinear programming techniques. Usually some form of computer (more advanced than a programmable calculator) is required. Therefore, parameter estimation during field testing is difficult if not impossible, which is a major short coming. For example, many consultants and users specify multiple tests for performance compliance testing, with limited variability among test results. If the parameters are not estimated in the field, it is impossible to know in the field if adequate testing has been performed.

The objective of this paper is to demonstrate the use of the exponential parameter estimation technique using simple nonlinear programming techniques. The techniques presented here are quite simple and can be programmed on an advanced programmable calculator, such as the Texas Instruments TI-59, or similar calculator. The techniques presented here will allow field investigators to perform the exponential parameter estimation technique in the field.

Nonlinear Programing

There are many techniques for nonlinear programing and a rigorous or lengthy review would not be appropriate here. The work of Beveridge and Schechter (3) or Kuester and Mize (11) should be consulted for further information. In general there are three broad classifications of nonlinear programing techniques: (1) Gradient techniques; (2) linearization techniques; and (3) pattern search techniques. Occasionally two of the methods are combined to make a more efficient algorithm. In general, no single technique is universally applicable to all types of problems, nor is any single method most efficient in all cases. However, many investigators find that it is convenient to use one technique for a broad variety of problems, because the penalty of computational inefficiency is often less severe than the difficulty encountered in finding and implementing the most computationally efficient technique. The first technique proposed here was originally presented by Box (4) and is called the Complex Method. Additionally the method can handle constraints, and because of this ability, the technique is suitable to a large variety of problems, and has been used by the first writer (14) for estimating kinetic coefficients and optimal controller parameters, and by Craig, Meredith, and Middleton (8) for optimal activated sludge process design. Only a brief review of the technique will be given, since lengthy explanations are available elsewhere. Additionally, the explanation of the techniques will be specific for DO parameter estimation.

Almost all techniques evaluate a sum of squares objective function defined as follows:

$$\text{error} = \sum_{j=1}^{m} [C_j - C(t_j)]^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

in which error = sum of squares error; m = number of data points; C_j = measure value of C at time = t_j; and $C(t_j)$ = calculated value of C at time = t_j.

Complex Method

The complex procedure begins by evaluating the error for four initial sets of estimates for the parameters $K_L a$, C_∞^*, and C_0. Since there are no unfeasible points, the initial set of estimates can be chosen randomly, or the initial sets can be estimated from one of the other DO parameter estimation techniques. Each initial parameter estimate should be unique. Speed of convergence is in part determined by the initial estimates; better initial estimates insure more rapid convergence.

One of the initial four sets of estimates must be the poorest, having the greatest error, and becomes the rejected set. The centroid of the remaining three sets of parameter estimates is calculated in order to project the next set of parameter estimates. In Cartesian coordinates, the coordinates of the centroid are obtained by averaging the remaining three estimates for each

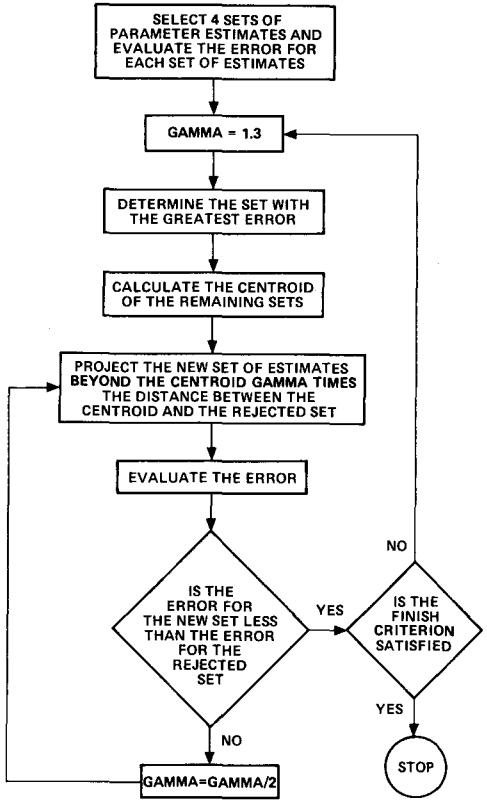

FIG. 1.—Flow Chart for Complex Method

parameter. The new set of parameter estimates is obtained by projecting from each rejected parameter estimate through the centroid a specific distance. The new parameter estimate must be obtained by projecting through the centroid since the optimal estimates may be outside the space contained within the remaining three parameter estimates. The original projection distance beyond the centroid, called gamma, is selected as 1.3 times the distance from the rejected parameter estimate to the centroid. The ratio of 1.3 was originally recommended by Box (4) and works well for this application. The error for a new set of parameter estimates is also calculated by Eq. 4.

If the error for the new set of estimates is less than the error for the rejected set, the new set of estimates replaces the rejected set. The technique now repeats by selecting the next set of parameter estimates with the highest sum of squares error for replacement. Conversely, if the error for the new set of estimates is greater than or equal to the error of the rejected set of estimates, the projection distance, gamma, is reduced by a factor of two and a second, new set of parameter estimates is calculated by projecting from the original rejected set beyond the centroid of the remaining three sets of estimates. This process is repeated until a set of parameter estimates is obtained which has lower error than the original rejected set. Once a new set of estimates is obtained, the technique repeats by selecting the next worst set.

This process is continued until a pre-established termination or finish criterion is obtained. One or more of several finish criteria can be selected. If the technique is implemented using some higher computer language such as FORTRAN, it is desirable to specify a maximum number of interations in addition to an error improvement criterion, which is the preferred termination method. An error improvement finish criterion can be specified by terminating the search in the event that the error is only improved by some specified percent for more than a specified number of iterations. This condition will occur when the four sets of parameter estimates converge to the optimal values. A programmable calculator is ideally suited for evaluating finish criteria. The calculator can be stopped and the convergence of the parameter estimates can be evaluated; if the estimates are unacceptable, the program is restarted. Fig. 1 is an information flow diagram of the complex technique.

Numerical Example

To illustrate the technique a numerical example is provided. Table 1 shows a set of concentration versus time data which was collected from a nonsteady state reaeration test in the UCLA Water Quality Laboratory. Table 2 shows the initial parameter estimates, the first five new sets of estimates, errors, and the converged set of estimates.

The first four sets of estimates were "guessed" from the data and any a priori knowledge of the system. For example, it can be observed from the data that C_∞^* is approx 7.5 mg/L. From this information $K_L a$ can be approximated from the "time constant method" noted by Gilbert and Libby (8). The initial DO deficit ($C_\infty^* - C_0$) will be decreased by approx 63% during one time constant, or $K_L a^{-1}$ units of time. For the data shown in Table 1, the initial deficit is approx 7.5 mg/L, which was reduced by 63% in approx 8 min. Therefore a good initial guess for $K_L a$ is approx 0.124 min^{-1}. The remaining three sets

of data were guessed to provide a scattering of values around the first guess.

The worst error is for set 3, which is rejected first. The new set of estimates is calculated by projecting through the centroid with $\gamma = 1.3$. For example, the calculation of the new estimate of $K_L a$ is as follows:

$$\text{Centroid} = \frac{(0.125 + 0.131 + 0.109)}{3} = 0.122 \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$\bar{K}_L a = \gamma(0.122 - 0.141) + 0.122 = 0.0973 \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

In a similar manner, new values, C_∞^*, and C_0, are estimated. Since there was no improvement in the error for $\gamma = 1.3$, it is reduced by two fold and the estimates are recalculated until an improved set is obtained.

It can be observed that the technique converged to within ±0.002 units for $\bar{K}_L a$ by iteration 25. Very little improvement in the error was obtained during the next 13 iterations, and the search was terminated.

TABLE 1.—Unsteady-State Reaeration Data

Time, in minutes (1)	DO concentration, in milligrams per liter (2)
0.	0.
1.8	1.39
3.8	2.73
5.8	3.80
6.8	4.32
7.8	4.62
8.8	5.02
9.8	5.32
11.8	5.87
13.8	6.24
15.8	6.58
17.8	6.91
19.8	7.13
21.8	7.20
23.8	7.23
25.8	7.41
27.8	7.48
29.8	7.56

Programmable Calculator Procedure

Fig. 2 shows the coding for the search procedure using the TI-59 calculator. Seventy memories and 378 program steps are required. Table 3 lists the procedure to execute the program. The program has sufficient space to accomodate up to 18 pairs of data points. The program requires approx 30 min to converge which is rapid enough to allow the program to be used in the field. A printer for the calculator is desirable, but not required. Undoubtedly the procedure can be implemented on other types of programmable calculators also. Table 4 shows the memory location used in the search procedure.

The complex method can also be used to estimate the parameters for the best-fit log deficit procedure. To implement the technique the TI-59 is programmed to search for $\bar{C}_\infty^*$ by the complex technique and to calculate $\bar{C}_0$ and $\bar{K}_L a$ by simple linear regression.

TABLE 2.—Summary of Exponential Search Program Using Complex Method

Set number (1)	Parameter Estimates $\bar{K}_L a$ (2)	Parameter Estimates $\bar{C}_\infty^*$ (3)	Parameter Estimates $\bar{C}_0$ (4)	Centroid $\bar{K}_L a$ (5)	Centroid $\bar{C}_\infty^*$ (6)	Centroid $\bar{C}_0$ (7)	Error (8)	Comments (9)
1	0.125	7.51	0.				0.3459	First guess
2	0.131	7.61	−0.11				0.2650	Second guess
3	0.141	7.71	0.12				2.375	Third guess
4	0.109	7.81	0.21				0.2770	Fourth guess
				0.122	7.64	0.033		Set 3 rejected
	0.0973	7.55	−0.080				>2.375	No improvement
5	0.110	7.59	−0.024				1.545	
				0.122	7.64	0.033		Set 5 rejected
	0.138	7.71	0.107				>1.545	No improvement
6	0.130	7.67	0.070				0.5570	
				0.122	7.64	0.033		Set 6 rejected
	0.114	7.60	−0.0151				>0.5570	No improvement
7	0.117	7.62	0.00900				0.3943	
				0.122	7.64	0.033		Set 7 rejected
	0.129	7.67	0.0642				>0.3943	No improvement
8	0.125	7.65	0.0486				0.2091	
				0.122	7.69	0.05		Set 1 rejected
	0.118	7.92	0.115				>0.2091	No improvement
9	0.120	7.81	0.0825				0.1784	
				0.125	7.69	0.0070		Set 4 rejected
25	0.121	7.72	−0.081				0.05789	Set 4 rejected
							0.05789	Set 4 rejected
38	0.118	7.80	−0.078				0.03920	

Linearization by Taylor Series

The oxygen transfer model shown in Eq. 1 can also be linearized using a Taylor series expansion of the model about some initial parameter estimate. The Taylor series expansion can be truncated after the first derivative, resulting in a linear approximation to the nonlinear transfer model. Linear least squares can then be used to approximate the linear model in successive steps until convergence is obtained. The method is reviewed generally by Draper and Smith (1) and specifically for oxygen transfer applications by Baillod and the second writer (9).

The linearization technique can be described most simply by writing the model in terms of three arbitrary parameters, as follows:

$$C = K_1 - (K_1 - K_2)e^{(-K_3 t)}$$

```
000  76 LBL
001  23 LNX
002  43 RCL
003  00  00
004  42 STO
005  08  08
006  71 SBR
007  79  x
008  00  0
009  42 STO
010  10  10
011  53  (
012  53  (
013  73 RC*
014  04  04
015  65  ×
016  73 RC*
017  01  01
018  94 +/-
019  54  )
020  22 INV
021  23 LNX
022  65  ×
023  53  (
024  73 RC*
025  05  05
026  75  -
027  73 RC*
028  06  06
029  54  )
030  94 +/-
031  85  +
032  73 RC*
033  05  05
034  75  -
035  73 RC*
036  02  02
037  54  )
038  22 INV
039  87 IFF
040  01  01
041  00  00
042  44  44
043  99 PRT
044  33 X²
045  44 SUM
046  10  10
047  69 DP
048  21  21
049  69 DP
050  22  22
051  97 DSZ
052  08  08
053  00  00
054  11  11
055  92 RTN
056  76 LBL
057  58 FIX
058  05  5
059  04  4
060  42 STO
061  04  04
062  05  5
063  09  9
064  42 STO
065  05  05
066  06  6
067  04  4
068  42 STO
069  06  06
070  06  6
071  09  9
072  42 STO
073  07  07
074  76 LBL
075  79  x
076  01  1
077  01  1
078  42 STO
079  01  01
080  85  +
081  43 RCL
082  00  00
083  95  =
084  42 STO
085  02  02
086  92 RTN
087  76 LBL
088  89  π
089  85  +
090  43 RCL
091  09  09
092  95  =
093  42 STO
094  01  01
095  92 RTN
096  76 LBL
097  60 DEG
098  04  4
099  42 STO
100  03  03
101  00  0
102  42 STO
103  01  01
104  43 RCL
105  08  08
106  85  +
107  01  1
108  95  =
109  42 STO
110  02  02
111  73 RC*
112  02  02
113  44 SUM
114  01  01
115  69 DP
116  22  22
117  97 DSZ
118  03  03
119  01  01
120  11  11
121  43 RCL
122  08  08
123  85  +
124  43 RCL
125  09  09
126  95  =
127  42 STO
128  02  02
129  53  (
130  53  (
131  43 RCL
132  01  01
133  75  -
134  73 RC*
135  02  02
136  54  )
137  55  ÷
138  03  3
139  54  )
140  72 ST*
141  08  08
142  75  -
143  73 RC*
144  02  02
145  95  =
146  65  ×
147  43 RCL
148  49  49
149  95  =
150  74 SM*
151  08  08
152  92 RTN
153  76 LBL
154  16 A'
155  47 CMS
156  42 STO
157  00  00
158  76 LBL
159  10 E'
160  71 SBR
161  58 FIX
162  04  4
163  42 STO
164  03  03
165  91 R/S
166  76 LBL
167  11  A
168  72 ST*
169  01  01
170  69 DP
171  21  21
172  91 R/S
173  76 LBL
174  12  B
175  72 ST*
176  02  02
177  69 DP
178  22  22
179  91 R/S
180  76 LBL
181  13  C
182  72 ST*
183  04  04
184  91 R/S
185  76 LBL
186  14  D
187  72 ST*
188  05  05
189  91 R/S
190  76 LBL
191  15  E
192  72 ST*
193  06  06
194  71 SBR
195  23 LNX
196  43 RCL
197  10  10
```

FIG. 2.—Coding for Complex Method


```
198  99 PRT
199  72 ST*
200  07  07
201  69 DP
202  34  34
203  69 DP
204  35  35
205  69 DP
206  36  36
207  69 DP
208  37  37
209  97 DSZ
210  03  03
211  01  01
212  79  79
213  01  1
214  93  .
215  03  3
216  42 STO
217  49  49
218  06  6
219  06  6
220  42 STO
221  01  01
222  03  3
223  42 STO
224  03  03
225  01  1
226  42 STO
227  09  09
228  73 RC*
229  01  01
230  32 X:T
231  69 DP
232  21  21
233  73 RC*
234  01  01
235  77  GE
236  02  02
237  45  45
238  97 DSZ
239  03  03
240  02  02
241  31  31
242  61 GTO
243  02  02
244  59  59
245  53  (
246  05  5
247  75  -
248  43 RCL
249  03  03
250  54  )
251  42 STO
252  09  09
253  73 RC*
254  01  01
255  32 X:T
256  61 GTO
257  02  02
258  38  38
259  05  5
260  00  0
261  42 STO
262  08  08
263  71 SBR
264  60 DEG
265  05  5
266  05  5
267  42 STO
268  08  08
269  71 SBR
270  60 DEG
271  06  6
272  00  0
273  42 STO
274  08  08
275  71 SBR
276  60 DEG
277  71 SBR
278  23 LNX
279  43 RCL
280  10  10
281  32 X:T
282  43 RCL
283  09  09
284  85  +
285  06  6
286  05  5
287  95  =
288  42 STO
289  65  65
290  73 RC*
291  65  65
292  77  GE
293  03  03
294  02  02
295  02  2
296  22 INV
297  49 PRD
298  49  49
299  61 GTO
300  02  02
301  59  59
302  05  5
303  00  0
304  71 SBR
305  89  π
306  43 RCL
307  50  50
308  72 ST*
309  01  01
310  05  5
311  05  5
312  71 SBR
313  89  π
314  43 RCL
315  55  55
316  72 ST*
317  01  01
318  06  6
319  00  0
320  71 SBR
321  89  π
322  43 RCL
323  60  60
324  72 ST*
325  01  01
326  06  6
327  05  5
328  71 SBR
329  89  π
330  43 RCL
331  10  10
332  99 PRT
333  72 ST*
334  01  01
335  61 GTO
336  02  02
337  13  13
338  76 LBL
339  17 B'
340  86 STF
341  01  01
342  71 SBR
343  23 LNX
344  22 INV
345  86 STF
346  01  01
347  91 R/S
348  76 LBL
349  18 C'
350  61 GTO
351  02  02
352  13  13
353  91 R/S
354  76 LBL
355  19 D'
356  43 RCL
357  00  00
358  32 X:T
359  71 SBR
360  79  x
361  73 RC*
362  01  01
363  99 PRT
364  73 RC*
365  02  02
366  99 PRT
367  69 DP
368  21  21
369  69 DP
370  22  22
371  97 DSZ
372  00  00
373  03  03
374  61  61
375  32 X:T
376  42 STO
377  00  00
378  91 R/S
```

FIG. 2.—*Continued*

in which $K_1 = \bar{C}^*_\infty$; $K_2 = C_0$; and $K_3 = K_L a$. The partial derivatives of the model with respect to each parameter, are as follows:

$$Z_1 = \frac{\partial C}{\partial K_1} = 1 - e^{(-K_3 t)} \quad \ldots\ldots (8)$$

$$Z_2 = \frac{\partial C}{\partial K_2} = e^{(-K_3 t)} \quad \ldots\ldots (9)$$

$$Z_3 = \frac{\partial C}{\partial K_3} = t(K_1 - K_2)e^{(-K_3 t)} \quad \ldots\ldots (10)$$

The Taylor series expansions of Eq. 7 about the parameters becomes

$$C_{obs} = C^o_{calc} + Z^o_1(K_1 - K^o_1) + Z^o_2(K_2 - K^o_2) + Z^o_3(K_3 - K^o_3) \quad \ldots\ldots (11)$$

in which C_{obs} = observed DO concentration values; and C^o_{calc} = calculated

TABLE 3.—Calculator Entry Instruction for Exponential Search Program Using Complex Method

Data entry (1)	Program-key (2)	Function (3)	Display (4)
n	A′	Initializes calculator and enters number of data pairs	4
t_i	A	Enter time of each data pair (data is entered in pairs)	t_i
C_i	B	Enter DO concentration of each pair	C_i
$\bar{K}_L a$	C	Initial estimate of $K_L a$ (initial estimates are entered in sets)	$\bar{K}_L a$
$\bar{C}^*_\infty$	D	Initial estimate of C^*_∞	$\bar{C}^*_\infty$
$\bar{C}_0$	E	Initial estimate of C_0	$\bar{C}_0$
-	B′	Instruction for calculating and printing residuals	c
-	C′	Restart search after loss of display contents or program location	c
-	D′	Instruction for printing data	c
-	E′	Reset calculator for repeating search for same data set with new initial guesses	4
-	R/S	Stops program for inspection of parameter estimates. Reentering display contents and restoring current program location permits restart with R/S	

DO concentration values using the parameter values K^o_i; and the superscript ^{o} indicates the values of the parameters about which the Taylor expansion occurs. Eq. 11 can be written in the following linear form:

$$W^o = b_1 Z^o_1 + b_2 Z^o_2 + b_3 Z^o_3 \quad \ldots\ldots (12)$$

in which $W^o = C_{obs} - C^o_{calc}$; $b_i = K_i - K^o_i$; and Z^o_i = partial derivative of the model evaluated at the parameter values K^o_i.

To begin the estimation procedure, initial values of the model parameters,

K^o_i, must be provided. These initial parameter values are used to calculate the values of W^o and Z^o_i in Eq. 12. Because Eq. 12 is linear in the parameters, b_i, linear least squares (multiple linear regression) can be used to calculate estimates of b_i. The least squares estimates of b_i provide updated estimates of the model parameters, K_i, by the following relationship:

$$K_i = b_i + K^o_i \quad \ldots\ldots (13)$$

in which K^o_i = the prior estimate of the parameters; and K_i = the updated estimates. The values of b_i can be viewed as corrections applied to the prior estimates of the parameters.

Since the initial parameter estimates are not necessarily correct, several iterations through the previous equation must be performed until the corrections, b_i, approach zero. For this case, convergence is usually obtained in only five or six iterations.

The parameter estimates for Eq. 12 must be calculated from the least squares

TABLE 4.—Memory Location for TI-59 Complex Method

Register number (1)	Storage value (2)
0–9	Counters, pointers and indirect address indices used in the program
10	New error
11–48	C versus t data starting with n values of t at location 11, following with n values of C at the end of the t data
49	Gamma
50	New $\bar{K}_L a$
51–54	$\bar{K}_L a$ (for sets one to four in descending order)
55	New $\bar{C}^*_\infty$
56–59	$\bar{C}^*_\infty$'s (for sets one to four in descending order)
60	New $\bar{C}_0$
61–64	$\bar{C}_0$'s (for sets one to four in descending order)
65	New error
66–69	Errors (for sets one to four in descending order)

estimates. Omitting the superscripts, the sum of squares function, S, to be minimized is

$$S = \Sigma(W - b_1 Z_1 - b_2 Z_2 - b_3 Z_3)^2 \quad \ldots\ldots (14)$$

in which S = the sum of squares; and the summation is performed over all the values of the concentration versus time data. Minimization of S with respect to the parameters b_i leads to the following set of normal equations:

$$b_1 \Sigma Z_1^2 + b_2 \Sigma Z_1 Z_2 + b_3 \Sigma Z_1 Z_3 = \Sigma W Z_1 \quad \ldots\ldots (15)$$

$$b_1 \Sigma Z_1 Z_2 + b_2 \Sigma Z_2^2 + b_3 \Sigma Z_2 Z_3 = \Sigma W Z_2 \quad \ldots\ldots (16)$$

$$b_1 \Sigma Z_1 Z_3 + b_2 \Sigma Z_2 Z_3 + b_3 \Sigma Z_3^3 = \Sigma W Z_3 \quad \ldots\ldots (17)$$

This set of equations can be written more conveniently as follows:

$$a_{11} b_1 + a_{12} b_2 + a_{13} b_3 = c_1 \quad \ldots\ldots (18)$$

```
000  76 LBL
001  58 FIX
002  01  1
003  01  1
004  42 STO
005  01  01
006  85  +
007  43 RCL
008  00  00
009  42 STO
010  03  03
011  95  =
012  42 STO
013  02  02
014  92 RTN
015  76 LBL
016  16 A'
017  47 CMS
018  42 STO
019  00  00
020  71 SBR
021  58 FIX
022  91 R/S
023  76 LBL
024  11  A
025  72 ST*
026  01  01
027  69 DP
028  21  21
029  91 R/S
030  76 LBL
031  12  B
032  72 ST*
033  02  02
034  69 DP
035  22  22
036  91 R/S
037  76 LBL
038  13  C
039  42 STO
040  04  04
041  91 R/S
042  76 LBL
043  14  D
044  42 STO
045  05  05
046  91 R/S
047  76 LBL
048  15  E
049  42 STO
050  06  06
051  71 SBR
052  58 FIX
053  00  0
054  42 STO
055  07  07
056  42 STO
057  08  08
058  42 STO
059  09  09
060  42 STO
061  10  10
062  42 STO
063  55  55
064  42 STO
065  56  56
066  42 STO
067  60  60
068  42 STO
069  61  61
070  42 STO
071  62  62
072  71 SBR
073  23 LNX
074  94 +/-
075  85  +
076  01  1
077  95  =
078  42 STO
079  57  57
080  53  (
081  43 RCL
082  05  05
083  75  -
084  43 RCL
085  06  06
086  54  )
087  65  ×
088  43 RCL
089  58  58
090  65  ×
091  73 RC*
092  01  01
093  95  =
094  42 STO
095  59  59
096  43 RCL
097  57  57
098  33 X²
099  44 SUM
100  07  07
101  43 RCL
102  57  57
103  65  ×
104  43 RCL
105  58  58
106  95  =
107  44 SUM
108  08  08
109  43 RCL
110  57  57
111  65  ×
112  43 RCL
113  59  59
114  95  =
115  44 SUM
116  09  09
117  43 RCL
118  58  58
119  33 X²
120  44 SUM
121  10  10
122  43 RCL
123  58  58
124  65  ×
125  43 RCL
126  59  59
127  95  =
128  44 SUM
129  55  55
130  43 RCL
131  59  59
132  33 X²
133  44 SUM
134  56  56
135  71 SBR
136  44 SUM
137  65  ×
138  43 RCL
139  57  57
140  95  =
141  44 SUM
142  60  60
143  43 RCL
144  54  54
145  65  ×
146  43 RCL
147  58  58
148  95  =
149  44 SUM
150  61  61
151  43 RCL
152  54  54
153  65  ×
154  43 RCL
155  59  59
156  95  =
157  44 SUM
158  62  62
159  69 DP
160  21  21
161  69 DP
162  22  22
163  97 DSZ
164  03  03
165  00  00
166  72  72
167  43 RCL
168  07  07
169  65  ×
170  43 RCL
171  10  10
172  75  -
173  43 RCL
174  08  08
175  33 X²
176  95  =
177  42 STO
178  63  63
179  43 RCL
180  07  07
181  65  ×
182  43 RCL
183  62  62
184  75  -
185  43 RCL
186  09  09
187  65  ×
188  43 RCL
189  60  60
190  95  =
191  42 STO
192  64  64
193  43 RCL
194  07  07
195  65  ×
196  43 RCL
197  55  55
198  75  -
199  43 RCL
200  09  09
```

FIG. 3.—Coding for Linearization Method


```
201  65  ×
202  43 RCL
203  08  08
204  95  =
205  42 STO
206  65  65
207  43 RCL
208  56  56
209  65  ×
210  43 RCL
211  07  07
212  75  -
213  43 RCL
214  09  09
215  33 X²
216  95  =
217  42 STO
218  66  66
219  43 RCL
220  07  07
221  65  ×
222  43 RCL
223  61  61
224  75  -
225  43 RCL
226  08  08
227  65  ×
228  43 RCL
229  60  60
230  95  =
231  42 STO
232  67  67
233  53  (
234  43 RCL
235  63  63
236  65  ×
237  43 RCL
238  64  64
239  75  -
240  43 RCL
241  65  65
242  65  ×
243  43 RCL
244  67  67
245  54  )
246  55  ÷
247  53  (
248  43 RCL
249  63  63
250  65  ×
251  43 RCL
252  66  66
253  75  -
254  43 RCL
255  65  65
256  33 X²
257  54  )
258  95  =
259  99 PRT
260  42 STO
261  69  69
262  53  (
263  43 RCL
264  67  67
265  75  -
266  43 RCL
267  65  65
268  65  ×
269  43 RCL
270  69  69
271  54  )
272  55  ÷
273  43 RCL
274  63  63
275  95  =
276  99 PRT
277  42 STO
278  68  68
279  53  (
280  43 RCL
281  60  60
282  75  -
283  43 RCL
284  08  08
285  65  ×
286  43 RCL
287  68  68
288  75  -
289  43 RCL
290  09  09
291  65  ×
292  43 RCL
293  69  69
294  54  )
295  55  ÷
296  43 RCL
297  07  07
298  95  =
299  99 PRT
300  44 SUM
301  05  05
302  43 RCL
303  68  68
304  44 SUM
305  06  06
306  43 RCL
307  69  69
308  44 SUM
309  04  04
310  98 ADV
311  61 GTO
312  00  00
313  51  51
314  76 LBL
315  23 LNX
316  53  (
317  73 RC*
318  01  01
319  65  ×
320  43 RCL
321  04  04
322  94 +/-
323  54  )
324  22 INV
325  23 LNX
326  42 STO
327  58  58
328  92 RTN
329  76 LBL
330  44 SUM
331  53  (
332  73 RC*
333  02  02
334  75  -
335  43 RCL
336  05  05
337  85  +
338  53  (
339  43 RCL
340  05  05
341  75  -
342  43 RCL
343  06  06
344  54  )
345  65  ×
346  43 RCL
347  58  58
348  54  )
349  42 STO
350  54  54
351  92 RTN
352  76 LBL
353  17 B'
354  00  0
355  42 STO
356  08  08
357  71 SBR
358  58 FIX
359  71 SBR
360  23 LNX
361  42 STO
362  58  58
363  71 SBR
364  44 SUM
365  99 PRT
366  33 X²
367  44 SUM
368  08  08
369  69 DP
370  21  21
371  69 DP
372  22  22
373  97 DSZ
374  03  03
375  03  03
376  59  59
377  43 RCL
378  08  08
379  99 PRT
380  91 R/S
381  76 LBL
382  19 D'
383  71 SBR
384  58 FIX
385  73 RC*
386  01  01
387  99 PRT
388  69 DP
389  21  21
390  73 RC*
391  02  02
392  99 PRT
393  69 DP
394  22  22
395  97 DSZ
396  03  03
397  03  03
398  85  85
399  91 R/S
```

FIG. 3.—*Continued*

$$a_{22}b_1 + a_{22}b_2 + a_{23}b_3 = c_2 \quad (19)$$

$$a_{31}b_1 + a_{32}b_2 + a_{33}b_3 = c_3 \quad (20)$$

in which $a_{11} = \Sigma Z_1^2$ (21)

$$a_{12} = a_{21} = \Sigma Z_1 Z_2 \quad (22)$$

$$a_{13} = a_{31} = \Sigma Z_1 Z_3 \quad (23)$$

$$a_{22} = \Sigma Z_2^2 \quad (24)$$

$$a_{23} = a_{32} = \Sigma Z_2 Z_3 \quad (25)$$

$$a_{33} = \Sigma Z_3^2 \quad (26)$$

$$c_1 = \Sigma WZ_1 \quad (27)$$

$$c_2 = \Sigma WZ_2 \quad (28)$$

and $c_3 = \Sigma WZ_3$ (29)

Solution of Eq. 18–20 gives the following explicit set of equations for the b_i terms:

$$b_3 = \frac{(d_1 d_2 - d_3 d_5)}{(d_1 d_4 - d_3 d_3)} \quad (30)$$

$$b_2 = \frac{(d_5 - d_3 b_3)}{d_1} \quad (31)$$

$$b_1 = \frac{(c_1 - a_{12} b_2 - a_{13} b_3)}{a_{11}} \quad (32)$$

in which $d_1 = a_{22}a_{11} - a_{12}a_{12}$ (33)

$$d_2 = a_{11}c_3 - a_{13}c_1 \quad (34)$$

$$d_3 = a_{11}a_{23} - a_{13}a_{12} \quad (35)$$

$$d_4 = a_{11}a_{33} - a_{13}a_{13} \quad (36)$$

and $d_5 = a_{11}c_2 - a_{12}c_1$ (37)

Fig. 3 shows the TI-59 coding for the solution of this set of equations. The calculator is programmed to print the values of b_i and continue iterating until the user stops the program. Table 5 shows the instructions and Table 6 lists the storage locations. Table 7 shows the calculator output for the data presented in Table 1, with initial guess for $K_L a$, $\bar{C}_\infty^*$, and C_0 as 0.125 m^{-1}, 7.51 mg/L and 0.0 mg/L, respectively. Convergence is rapidly obtained in five or six iterations.

Precision of Parameter Estimates

Unfortunately a rigorous analysis of the precision of parameter estimates obtained from nonlinear programming and nonlinear regression techniques does not exist. This occurs because it is not possible to apply probability theory

to a general nonlinear model. Nevertheless it is possible to calculate the precision of the parameter estimates using methods for linear regression. For the Complex technique it is possible to calculate the standard errors of the parameter estimates using methods developed for linear regression; for the linearization technique it is possible to calculate the standard errors of the parameter estimates from the linearized, Taylor series model. These indicators of precision do not have the same rigorous statistical foundation as the analogous indicators for linear regression; however, they are useful to estimate the confidence limits on the parameter estimates, and to compare the precision of different data sets, and testing methods.

For the Complex technique the estimate of the standard error of $\bar{K}_L a$ can be calculated as follows:

$$SE_{\bar{K}_L a} = \sqrt{\frac{RMS}{s_t^2 (n-1)}} \quad (38)$$

in which $SE_{\bar{K}_L a}$ = estimate of the standard error for $\bar{K}_L a$, RMS = residual

TABLE 5.—Calculator Entry Instructions for Exponential Search Program Using Linearization Method

Data entry (1)	Program-key (2)	Function (3)	Display (4)
n	A′	Initializes calculator and enters number of data pairs	
t_i	A	Enter time for each data pair (data is entered in pairs)	t_i
C_i	B	Enter DO concentration of each pair	C_i
$\bar{K}_L a$	C	Initial estimate of $\bar{K}_L a$	$\bar{K}_L a$
$\bar{C}_\infty^*$	D	Initial estimate of $\bar{C}_\infty^*$	$\bar{C}_\infty^*$
$\bar{C}_0$	E	Initial estimate of C_0	C_0
		Calculator will interate, printing the values of b_i, until stopped by the user	
-	B′	Instruction for calculating and printing the residuals	c
-	D′	Instruction for printing the data	
	R/S	Stops program for inspection of parameter estimates	

mean square of the nonlinear regression (equals the sum of squares divided by the degrees-of-freedom); s_t^2 = variance of the time data; and n = number of data points. The estimate of the standard error of $\bar{C}_\infty^*$ can be calculated in a similar fashion, as follows:

$$SE_{\bar{C}_\infty^*} \sqrt{\frac{RMS}{n} + \frac{RMS\, t_m^2}{S_t^2 (n-1)}} \quad (39)$$

in which $SE_{\bar{C}_\infty^*}$ = estimates of standard error of $\bar{C}_\infty^*$; and t_m = mean value of the time data.

For linearization procedure, the estimates of standard errors for the parameter

estimates can be calculated from the inverse of the coefficient matrix (Eqs. 18–20) and the residual mean square. The equations are as follows:

$$SE_{K_i} = \sqrt{\frac{E_{ii}\,RMS}{D}} \qquad (40)$$

in which SE_{K_i} = standard error of the parameter estimates K_i; E_{ii} = cofactors of a_{ii} in the coefficient matrix; and D = determinant of the coefficient matrix.

The TI-59 programs shown in Figs. 2 and 3 do not include the coding for calculating standard errors; however, it is not difficult to calculate the standard error manually by recalling the appropriate coefficients from the calculator memory. Alternatively, a second program could be written that could be read into memory after the techniques have converged and final parameter estimates are available.

TABLE 6.—Memory Locations for TI-59 Linearization Method

Register number (1)	Storage value (2)
0	Number of data pairs
1–3	Loop counters
4	$\bar{K}_L a$
5	$\bar{C}^*_\infty$
6	$\bar{C}_0$
7	a_{11}
8	a_{12}
9	a_{13}
10	a_{22}
11–53	C versus t data starting with n values of t at location 11, following with n values of C at end of t data
54	W_i
55	a_{23}
56	a_{33}
57	Z_1
58	Z_2
59	Z_3
60	C_1
61	C_2
62	C_3
63	d_1
64	d_2
65	d_3
66	d_4
67	d_5
68	b_2
69	b_3

Pitfalls of Nonlinear Programming

An important aspect of nonlinear programming is the possibility of obtaining local optima. Choosing a local optimum for the parameter estimates might produce

very different estimates for oxygen transfer than using the global optimum. Therefore it is common practice to repeat the search from several different starting locations. If the same estimates for several different sets of initial values of the parameter estimates are obtained, one generally assumes that the global optimum has been obtained.

A very good indicator of global optimum is the nature of the residual distribution. If the residuals are not randomly distributed with mean zero, the model is not valid, or a local optimum has been obtained by the nonlinear programming technique. When using nonlinear programming one must always be aware of the possibilities of local optima. The writers have observed local optima only with "noisy" data sets. Perhaps the occurrence of local optima is an indication of inadequate precision in data collection.

There are some guidelines for choosing initial parameter estimates for the Complex technique. No duplication should be made with any parameter estimates. Also the initial estimates should be chosen so that no one estimate is located at the centroid of the remaining estimates. For example, if initial estimates of C^*_∞ are chosen as 8.0, 8.5, 9.0, and 10.5, and if the third estimate (9.0) has the greatest error, the centroid of the remaining three points is also 9.0. Initial estimates such as these can result in reduced speed of convergence or inability to converge. One method of avoiding this possibility is to choose initial estimates with three significant figures. For example a better set of estimates than the previous set would be 8.01, 8.47, 9.02, and 10.46.

TABLE 7.—Summary of Exponential Search Using Linearization Method

Set number (1)	Parameter estimates			Corrections (b_i)		
	$\bar{K}_L a$ (2)	$\bar{C}^*_\infty$ (3)	$\bar{C}_0$ (4)	$\bar{K}_L a$ (5)	$\bar{C}^*_\infty$ (6)	$\bar{C}_0$ (7)
1	0.125	7.51	0.0	−0.0079	0.29	−0.056
2	0.117	7.79	−0.056	0.00057	0.0042	−0.0032
3	0.117	7.80	−0.058	8.8×10^{-6}	0.00018	0.0005
4	0.118	7.80	−0.059			

For the linearization technique one should choose the best possible estimate for the parameters, in order to assure convergence. For cases where very poor initial estimates of the parameters are made, the solution procedure may not converge. If this happens the program must be restarted using better estimates. The time constant method is often useful for obtaining initial estimates of the parameters.

Where parameters are being estimated for final design or for performance testing, several repetitions should be made having different initial estimates. If either technique does not converge to the same set of final estimates, the set of parameters which produces the lowest sums of squares, and the most uniform residuals should be selected.

Conclusions

Two nonlinear programming techniques have been presented which facilitate the use of the exponential DO parameter estimation technique for analyzing

nonsteady state reaeration data. Both nonlinear programming techniques are easy to use and can be used in the field with a programmable pocket calculator. It is shown that either technique can efficiently provide parameter estimates and that they both converge to the same final values. Both programs can accomodate an adequate number of observations. Use of either technique described here eliminates the need for estimating $\bar{C}^*_\infty$ from handbook or depth/correction methods, and also eliminates the need to truncate data when the DO concentration approaches saturation. With slight modification the techniques can be used for other nonlinear programing applications in environmental engineering, such as estimating biochemical oxygen demand rate coefficients and isotherm coefficients.

Acknowledgments

The development of the techniques presented here was stimulated by the writers' participation in the activities of the EPA-ASCE sponsored Subcommittee on Oxygen Transfer Standards. The work of the Subcommittee showed the need for improved oxygen transfer parameter estimation techniques, and especially showed the need for simple and portable methods which can be used in the field.

Appendix I.—References

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Appendix II.—Notation

The following symbols are used in this paper:

a = coefficients of normal equations matrix;
b = corrections for parameter estimates, K;
C = DO concentration at any time, in milligrams per liter;
C_0 = DO concentration at $t = 0$, in milligrams per liter;
C^*_∞ = saturation DO concentration, in milligrams per liter;
c, d = intermediate variables used in solution of normal equations;
D = determinate of coefficient matrix;
E = cofactor of coefficient matrix;
K = general parameter estimate;
$K_L a$ = apparent volumetric mass transfer coefficient (t^{-1});
t = time;
W = difference between expected and observed value of C;
Z = partial derivative of two film model taken with respect to parameter; and
γ = projection distance beyond centroid.

Superscripts

$^-$ = indicates statistical estimates for parameter; and
^{o} = indicates values of parameter about which expansion occurs.