

Calibration of Infrared Gas Analyzers for CO₂:
Mathematical Model and Experimental Results.¹

by

I. A. Tamas², N. S. Urquhart³, and J. L. Ozbun

Departments of Vegetable Crops and Biometry

Cornell University, Ithaca, New York 14850

ABSTRACT

CO₂ response curves for the Infrared Gas Analyzer were determined by adding small, measured amounts of CO₂ to a large volume of N₂ with a calibrated syringe. The gas circulated through the instrument and the response was evaluated after each addition. Several runs were made for each of the 300, 750, 1000, and 1500 ppm CO₂ full-scale ranges. For a given cell length, the curvature of the response curve increased with the full-scale CO₂ concentration. We deduce a mathematical model for the response curve and estimate its parameter from our data. Most data points deviate less than 1% of full-scale volume from the fitted curve, thus validating both the mathematical model and the precision of the instrument. We observe the role of this model in computer processing of large volumes of data generated by this instrument.

¹ Paper number 605. Department of Vegetable Crops, Cornell University, Ithaca, New York 14850.

² Present address: Department of Biology, Ithaca College, Ithaca, New York 14850.

³ Present address: Department of Experimental Statistics, New Mexico State University, Las Cruces, New Mexico 88001.

The response of the Infrared Gas Analyzer (IRGA) to CO_2 concentration is based on Beer's law (1), giving (2) a nonlinear relationship between the absorbed irradiation and CO_2 concentration. The full-scale response of the instrument can be made to correspond, within certain limits, to any desired CO_2 concentration with the instrument's gain control. The shape of the response curve depends on the full-scale CO_2 value and cell length. Normally the manufacturer furnishes a response curve for a single full-scale CO_2 concentration with each instrument. Adjustment of the instrument response to this curve requires a standard gas mixture of known CO_2 concentration. The measuring cell is flushed with the standard gas and the recorder pen is brought to the corresponding chart value with the instrument gain control, as determined from the response curve. Subsequently, the CO_2 concentration of unknown gas mixtures is determined by reading the obtained chart value against the manufacturer's curve.

The above described method of calibration and use is often inadequate for several reasons: i) Although special gas mixing pumps are now available for the preparation of accurate standards in the laboratory (3), instrument operators usually rely on commercially supplied standard gas mixtures. Our experience, as well as published reports (3), indicate that the commercial standards frequently show large differences between real and stated CO_2 concentrations. ii) Circumstances often require that the instrument be used at several different CO_2 concentration ranges. Reliance on the response curve, furnished by the manufacturers, restricts the user to a single CO_2 range. iii) Reading large numbers of CO_2 concentration values from the curve is a time consuming process and also subject to human error.

Our resolution of these difficulties involves an experimental procedure for calibrating the instrument and an associated mathematical model. The present paper

describes a simple method for the calibration of the IRGA, which enables the user to determine response curves accurately, without reliance on standard gas mixtures. The mathematical model is amenable to subsequent computer analysis of data without extensive manual translation of instrument readings into CO₂ concentrations.

EXPERIMENTAL

Apparatus. Two models, Nos. 215 and 315A, of the Beckman Infrared Gas Analyzer were used. Cell length in Model 215 was 25.4 cm. In Model 315A two cell lengths were tested in succession: 13.4 and 36.3 cm. The instrument was connected to a large flask and a Neptune membrane pump with glass and butyl rubber tubing, forming a closed system. Instrument response was recorded with a Leeds & Northrup Speedomax H recorder. CO₂ was injected into the system through a serum cap with a Becton-Dickinson syringe, equipped with a rubber plunger.

Gases. Prepurified nitrogen gas, containing less than 5 ppm CO₂, was obtained from the Air Reduction Co., New York, N. Y. Carbon dioxide gas, of purity 99.95%, was bought from the Cardox Company, Buffalo, N. Y.

Volume Determinations. The volume of the large flask was determined by filling with water from a volumetric flask at 20°C. Tubing and sample cell volume was calculated from internal dimensions. The total volume of the closed system was 13.4 liters. The volume of three 5 ml syringes was determined by dispensing water at 20°C.

Determination of the Response Curve. The instrument was first flushed with N₂ and the recorder was set to zero. Then an amount of CO₂, calculated to give the desired full-scale CO₂ concentration, was added to the closed system with a 5 ml syringe, and the recorder was set to full-scale with the instrument gain control. The gain position was recorded and the above process was repeated 3 or 4 times.

The mean of the obtained gain values was calculated and set on the instrument. The response curve of the instrument was generated by repeatedly adding small, identical aliquots of CO₂ to the system with a one ml syringe, and recording the instrument response after each addition. This was continued until the recorder reached the full-scale value. The volume of each aliquot was calculated by dividing the full-scale CO₂ concentration by the number of additions.

RESULTS AND DISCUSSION

Syringe Volumes. Three 5 ml syringes had mean volumes of 5.006, 5.004, and 5.003 ml, with 99% confidence intervals having lengths of 0.033 or less. Since the relative error was about 0.1%, the volumes of the 5 ml syringes were considered to be accurate. The calculation of the aliquot size, dispensed with the 1 ml syringe during the response curve determination, was based on the volume of the 5 ml syringe, as described in the preceding section.

The Model. Our objectives required that we establish an equational relationship between the instrument output (the chart reading), which we symbolize by x, and the carbon dioxide concentration, which we symbolize by y. In order to obtain a valid relationship, the model must reflect both the nature of the instrument and the way the experiment was conducted. The instrument response is based (1) on Beer's Law (2) which states that if monochromatic radiation of intensity I₀ passes through a solution for a distance of b, then the intensity of the absorbed radiation is given by

$$I_0(1 - e^{-acb}), \text{ frequently written as } I_0(1 - \exp[-acb]). \quad (1)$$

Here c is the concentration of the solution through which the radiation passes and a is the absorptivity, a constant which depends upon incident radiation and the absorbing solution. Since the instrument holds I₀, a, and b constant, changes in c lead to changes in the absorbed radiation. The instrument senses this by physi-

cally detecting the amount of heat produced by the absorbed radiation; it translates this into an electronic signal, which through electronic multiplication produces a response on a scale from 0 to 100 units. By varying the amount of multiplication (gain), any given concentration can be scaled to produce a reading of 100 units. Thus we reasoned that chart reading (x) should be related to carbon dioxide concentration (y) by the equation

$$x = 100 \frac{1 - \exp[-\beta y]}{1 - \exp[-\beta y_0]} \quad (2)$$

where x is the output chart reading, y is the associated CO₂ concentration, and y₀ is the CO₂ concentration scaled to produce a chart reading of 100.

This equation presents what we now assume to be the exact relation between chart reading and carbon dioxide concentration. Our data, however, does not exactly follow a smooth curve of this type because small unknown errors occurred each time an aliquot of carbon dioxide was introduced into the system. Thus instead of introducing a volume v of CO₂ each time, as intended, a volume v + ε was actually introduced. From the nature of the experiments and subsequent examination of the data, it seems plausible to assume that over a large number of trials these errors would average to zero and have constant variance. In fact, the data support the stronger assumption that the errors all follow the same normal probability distribution. The intent of successively adding the same volume, v, of CO₂ to the system was to get the data points (x₁, 1v), (x₂, 2v), (x₃, 3v), ..., (x_n, nv). Instead, because of the errors, we got (x₁^{*}, v + ε₁), (x₂^{*}, v + ε₁ + v + ε₂) = (x₂^{*}, 2v + ε₁ + ε₂), (x₃^{*}, 3v + ε₁ + ε₂ + ε₃), ..., (x_n^{*}, nv + ε₁ + ε₂ + ... + ε_n). Thus, our data are related by the equation

$$x_k^* = 100 \frac{\{1 - \exp[-\beta(kv + \epsilon_1 + \epsilon_2 + \dots + \epsilon_k)]\}}{1 - \exp[-\beta y_0]}, \quad k = 1, 2, \dots, n. \quad (3)$$

When this is solved so that the errors are additive, a statistically equivalent form is

$$y_0 \frac{\ln(1 - \alpha x_k^*)}{\ln(1 - 100\alpha)} = kv + \epsilon_1 + \epsilon_2 + \dots + \epsilon_k \quad \text{for } k = 1, 2, \dots, n \quad (4)$$

where $\alpha = (1 - \exp[-\beta y_0])/100$.

Estimation. In using the principle of least squares to estimate α , we took as our estimate that value of α , say $\hat{\alpha}$, which minimized the sum of squares of the estimated residuals, i.e. $\sum_{i=1}^n \hat{\epsilon}_i^2$. Notice that this is not the "standard" least squares fit because of the accumulative error structure. If d_i represents the distance of the i^{th} data point from the curve, standard least squares seeks estimates which minimize $\sum_{i=1}^n d_i^2$. Instead we had to minimize $d_1^2 + \sum_{i=2}^n (d_i - d_{i-1})^2$. The distinction between these two least squares approaches may seem academic; in our experience this was not the case. Careful lab work will keep the errors (our ϵ 's) small, but some will still be much larger than others. When a large error occurs, not only is the associated data point going to be some distance from the true curve, but several subsequent points are very likely to deviate from the true curve in the same direction. Thus, one moderately large deviation can pull the "standard" least squares fitted curve some distance away from the true curve. Our modified least squares procedure, which is merely one illustration of the generalized least squares theory (4), does not suffer from this criticism. The data from our single 750 ppm run and one of our 1500 ppm runs is plotted along with the respective estimated curves in Figure 1 to illustrate our previous point about the effect of the accumulative error structure. Note how the data points lie below and above the curves in groups. By contrast the consecutive differences from the estimated curve display no pattern in either sign or magnitude. For

example, the consecutive differences for the 750 ppm curve are: -0.28, 0.62, -2.05, 0.77, -1.25, 1.98, 0.65, -0.04, 2.28, 0.08, 1.16, -0.23, -0.85, 0.32, 1.67 -2.68, 0.76, 0.38.

Discussion. The results presented in Table I and Figure 1 support a consideration of two important points, the first concerning the shape of the curves and the second concerning precision. The shape, or more specifically the curvature, is governed by α or equivalently by β . The parameter α is bounded between 0.00 and 0.01, otherwise the natural log functions do not exist. Near $\alpha = 0.00$ the curves are nearly a straight line between (0,0) and (100, y_0), but as α moves through its permissible values toward its upper limit of 0.01, the curves dip further and further below the straight line. Thus, the fact that α has different values for the different conditions set out in Table I implies that accurate use of such instruments requires that a separate calibration be done for each condition. This differential curvature appears in Figure 1 where the curve for 750 ppm is almost a straight line, while the 1500 ppm curve is much more curved. From Table I you can see that only the full-scale volume differs for these two data sets. Again, this observation has a simple consequence: Accurate use of such instruments requires their careful calibration for the conditions under which they will be used.

The other point, concerning precision, relates to the last two columns of Table I. Originally the instrument was designed to give only a crude measurement of carbon dioxide concentration. Our results indicate that the instrument is precise, i.e. it produces responses with a high degree of internal agreement. In the column labeled maximum residual we present the greatest deviation of any of our data points from the estimated model, i.e., $\hat{\epsilon}_i$. In no case does this exceed 2% of full-scale volume, and is much less in most cases. A significant part of these deviations can be attributed to human error in various aspects of the experiment. The

last column in the table, labeled $\sqrt{\text{Average Squared Residual}}$, presents an index of the average deviation of the data points from the curve; naturally it is much less than the maximum deviation. 0.5% of full-scale volume serves as a practical upper bound. The repeatability on replicate runs provides us with further verification of precision. If the several runs are true replicates, the shape parameter should be the same for each of them. A statistical test of this fact gives no reason to doubt that the same parameter values underlay the several runs at 300 ppm full-scale volume; likewise, at 1500 ppm full-scale volume; ^{only} modest indication of inequality of parameter values exists at 1000 ppm full-scale volume, but since these were the first runs, this may be attributed to initial inexperience with the experimental techniques.

Modifications. How would the availability of several accurately evaluated CO₂ mixtures alter our comments? Or where, in view of our earlier comments, might we get such accurately evaluated mixtures? We have already proposed a method for calibrating an instrument. It could then be used to accurately evaluate the CO₂ content of available mixtures. These could be created easily and inexpensively by adding various amounts of pure CO₂ to small tanks of pure N₂. Thereafter these tanks could be used to check the calibration of an instrument or to recalibrate an instrument as needed. Some researchers (5) strongly recommend recalibrating an instrument after it has been moved or changed in any way.

The distinctive feature of our earlier model and the estimation of its parameters rested on the accumulative error structure. The availability of several mixtures, with accurately evaluated CO₂ contents, leads to only one change in our previous comments. Previously, we let d_i represent the distance of the i^{th} data point from the estimated curve. The generalized principle of least squares led to minimizing $d_1^2 + \sum_{i=2}^n (d_i - d_{i-1})^2$ for the accumulative error structure. If data

results from several separate gas mixtures with known CO₂ concentrations, the earlier accumulative error structure does not occur. Instead, each data point deviates from the curve independently from other data points. Except for this change, the same model applies. Now, however, the least squares principle requires that estimation be done so as to minimize $\sum_{i=1}^n d_i^2$ instead of the earlier expression. Computationally this requires changing only the minimize criterion in the routine set out in the appendix.

APPENDIX: COMPUTATION

This appendix sketches a computer routine which will estimate α for the accumulative error model and the changes necessary for the independent error model. It has been expressed as a FORTRAN IV subroutine because most people could use it as presented or in a slightly modified form. This routine has the variables N, X, Y, YZ, ACR, ALPHA, SSRES in its parameter vector; all are assumed to be real double precision variables except N which is an integer. X and Y are arrays containing the N pairs (X(I), Y(I)) of chart readings and CO₂ concentrations; they must be dimensioned in the calling program. YZ symbolizes y_0 , i.e. the curve must go through (100, y_0) and ACR symbolizes the minimum multiplicative factor by which ALPHA is changed in the search; .0001 is a reasonable value. The routine returns the estimate of α in ALPHA and the associated residual sum of squares in SSRES.

The minimization routine operates from the following observation: $0.00 \leq \alpha < 0.01$. At $\alpha = 0.00$ the curve degenerates into a straight line through (0,0) and (100, y_0), but as α increases to 0.01, the curve dips more and more. Thus the residual sum of squares decreases as α moves from 0.00 to the value, $\hat{\alpha}$, which minimizes the residual sum of squares; thereafter the residual sum of squares increases.

The routine takes .005 as an initial value for α ; thereafter the routine increases or decreases ALPHA away from this initial value (in progressively smaller steps) until the residual sum of squares ceases to increase. The routine follows:

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SUBROUTINE MIN(N,X,Y,YZ,ACR,ALPHA,SSRES)
REAL*8 X(N),Y(N),YZ,ALPHA,ACR,SSRES,K,RSS,R1,R2,R3
ALPHA=.005D0
K=1.D0
3 K=.1D0*K
4 R1=RSS(N,X,Y,YZ,(1.D0-K)*ALPHA)
  R2=RSS(N,X,Y,YZ,      ALPHA)
  R3=RSS(N,X,Y,YZ,(1.D0+K)*ALPHA)
  IF((R1.GT.R2).AND.(R2.GE.R3))GO TO 6
  IF((R1.LT.R2).AND.(R2.LT.R3))GO TO 5
C QUADRATIC INTERPOLATION FOR STRADDLED MINIMUM
  ALPHA=ALPHA*(1.D0+.5D0*K*(R1-R3)/(R1-R2-R2+R3))
  IF(K-ACR)7,7,3
5 ALPHA=(1.D0-K)*ALPHA
  GO TO 4
6 ALPHA=(1.D0+K)*ALPHA
  GO TO 4
7 SSRES=R2
  RETURN
  END

REAL FUNCTION RSS*8(N,X,Y,YZ,A)
REAL*8 X(N),Y(N),YZ,A
Y1=YZ*DLOG(1.D0-A*X(1))/DLOG(1.D0-100.D0*A)
RSS=(Y(1)-Y1)**2
IF(N.EQ.1)GO TO 1
DO 2 I=2,N
  Y2=Y1
  Y1=YZ*DLOG(1.D0-A*X(I))/DLOG(1.D0-100.D0*A)
C FOR NON-ACCUMULATIVE ERRORS,REPLACE NEXT STATEMENT BY RSS=RSS+(Y(I)-Y1)**2
2 RSS=RSS+((Y(I)-Y1)-(Y(I-1)-Y2))**2
1 RETURN
  END
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ACKNOWLEDGMENT

The authors wish to thank R. G. S. Bidwell for suggesting the experimental method used here; F. A. Martin for helpful discussions, and L. Turner for skillful technical assistance.

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TABLE I

ESTIMATES OF CURVATURE AND PRECISION OF CO₂ RESPONSE CURVES

Full Scale CO ₂ Conc. (ppm)	Instrument (Beckman No.)	Cell Length (cm)	Run	Estimate of α	Maximum Residual (ppm)	$\sqrt{\text{Ave. SquaredResidual}}$ (ppm)
300	315A	34.3	1	0.00499	5.0	1.7
			2	0.00577	2.0	1.0
			3	0.00539	1.8	1.0
			4	0.00519	2.2	0.8
			pooled	0.00536	5.0	1.2
750	315A	13.4	1	0.00469	2.7	1.3
1000	215	25.4	1	0.00664	5.2	2.4
			2	0.00729	7.9	3.6
			3	0.00691	6.7	3.6
			pooled	0.00693	9.3	3.3
1500	315A	13.4	1	0.00682	14.9	5.3
			2	0.00680	4.6	3.2
			3	0.00673	7.9	3.5
			pooled	0.00678	14.9	4.0