1. Initial guesses for R and Energy: $R := 1$ $Energy := -1$

2. Set up solution block:

Given

$$Energy = -.5 + \frac{1}{R} + \frac{\left[\left(1+\frac{1}{R}\right)\cdot\exp(-2\cdot R) - (1+R)\cdot\exp(-R) - \frac{1}{R}\right]}{\left[1+\left(1+R+\frac{R^2}{3}\right)\cdot\exp(-R)\right]}$$

$$\frac{d}{dR}\left[-.5 + \frac{1}{R} + \frac{\left[\left(1+\frac{1}{R}\right)\cdot\exp(-2\cdot R) - (1+R)\cdot\exp(-R) - \frac{1}{R}\right]}{\left[1+\left(1+R+\frac{R^2}{3}\right)\cdot\exp(-R)\right]}\right] = 0$$

3. Find R and Energy given the constraints above.

$$\begin{pmatrix} R \\ Energy \end{pmatrix} := Find(R, Energy) \qquad R = 2.4928 \qquad Energy = -0.5648$$

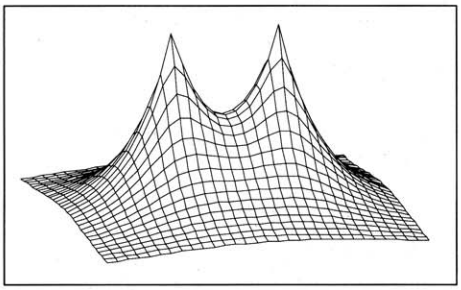
4. Display bonding molecular orbital:

Calculate over-lap integral: $S := \left(1+R+\frac{R^2}{3}\right)\cdot\exp(-R)$ $S = 0.46$

$N := 30$ $i := 0..N$ $j := 0..N$ $x_i := -2.5 + i\cdot\frac{7.5}{N}$ $y_j := -3 + j\cdot\frac{6}{N}$

$$\Psi(x,y) := \frac{\sqrt{\frac{1}{\pi}}\cdot\left[\exp\left[-\sqrt{(x^2+y^2)}\right] + \exp\left[-\sqrt{[(x-R)^2+y^2]}\right]\right]}{\sqrt{2+2\cdot S}}$$

$M_{(i,j)} := \Psi(x_i, y_j)$



M

Figure 3. Mathcad document for a molecular orbital calculation on the hydrogen molecule ion using unscaled hydrogen atom 1s orbitals.

include a palette of frequently used mathematical operators and a full set of Greek symbols.

The graphics package is versatile and easy to use. It supports the following.

- two-dimensional graphs
- surface plots
- the importation of graphics from other programs

In addition, release 3.0 has added a symbolic processor, making it possible to do symbolic operations on algebraic expressions, matrices, and vectors, as well as symbolic integration and differentiation of mathematical functions. To those of us who tackled undergraduate physical chemistry with slide rules and math tables, today's array of powerful computational aids is simply stunning.

Mathcad in Chemistry Calculations II Arrays

Zoran Zdravkovski
Institute of Chemistry, Cyril and Methodius University, POB 162 Skopje, Macedonia

The age of computerization has made certain algebraic tools readily available that had previously been neglected due to their nature. Probably the most illustrative example are the arrays. Nowadays, matrix algebra operations are integrated in many software packages, some of them supplied with different analytical instruments. Although very convenient, this does not enhance the students' knowledge and understanding of the limitations of these numerical methods.

On the other hand, teaching array operations with procedural languages does not necessarily simplify the problem. Students often get too involved with the programming and begin to loose the essence of the problem. The result is that students are unable to grasp the simplicity—and ultimately the full potential—of the methods. The equations- solving program Mathcad has greatly overcome this drawback; working with arrays becomes simple, straightforward, and user-friendly at the same time.

It is immediately clear that Mathcad is user-friendly by the manner in which arrays are displayed on the screen: The matrices are represented in two dimensions, just as we write them by hand. Also, all operations with them are just as natural.

For example, to obtain the inverse of the matrix $\mathbf{M}$ it's enough to write $\mathbf{M}^{-1}$. The transpose of the same matrix is $\mathbf{M}^{T}$, and the first column is $\mathbf{M}^{<1>}$, etc. It's obvious that this is the most natural way of representing those operations and functions, so one is free to devote the time to the problem—not the programing.

In a previous report in *this Journal* we discussed various chemistry problems using Mathcad (*10*). Now, we would like to illustrate the use of matrix algebra applied to various chemistry problems with the same software package.

Multicomponent Chemical Analysis

In many chemistry problems it is often necessary to solve a set of linear equations. For example, spectroscopic multicomponent analysis is based on the Beer–Lambert law. It yielded the following system of linear equations.

$$A_1 = k_{11}c_1 + k_{12}c_2 + \cdots k_{1n}c_n$$

Calculate the concentrations of each componenet of the basis of the following data obtained by infrared spectroscopy:

λ/μ	*p*-xylene εl/(L/mol)	*m*-xylene εl/(L/mol)	*o*-xylene εl/(L/mol)	ethyl-benzene εl/(L/mol)	Unknown Absorbances
12.5	1.502	0.0514	0	0.0408	0.1013
13.0	0.0261	1.1516	0	0.0820	0.09943
13.4	0.0342	0.0355	2.532	0.2933	0.2194
14.3	0.0340	0.0684	0	0.3470	0.03396

$$\mathbf{K} \equiv \begin{bmatrix} 1.5020 & 0.0514 & 0 & 0.0408 \\ 0.0261 & 1.1516 & 0 & 0.0820 \\ 0.0342 & 0.0355 & 2.532 & 0.2933 \\ 0.0340 & 0.0684 & 0 & 0.3470 \end{bmatrix} \qquad \mathbf{A} \equiv \begin{bmatrix} 0.10130 \\ 0.09943 \\ 0.21940 \\ 0.03396 \end{bmatrix}$$

Then the concentration matrix,

$$\mathbf{C} \equiv \mathbf{K}^{-1} \cdot \mathbf{A}$$

Mathcad calculates the concentrations.

$$C = \begin{bmatrix} 0.0627 \\ 0.0795 \\ 0.0759 \\ 0.0761 \end{bmatrix}$$

$C_0 = 0.0627$ concentration of *p*-xylene
$C_3 = 0.0761$ concentration of ethylbenzene

Figure 4. Mathcad's inout/output for the multicomponent analysis by infrared.

$$A_2 = k_{21}c_1 + k_{22}c_2 + \cdots k_{2n}c_n$$

$$\vdots$$

$$A_n = k_{n1}c_1 + k_{n2}c_2 + \cdots k_{nn}c_n$$

where A_i is the absorbance of the ith analytical wavelength; c_j is the concentration of the jth component; and k_{ij} is the proportionality constant.

In matrix notation this can be written as

$$\mathbf{A} = \mathbf{KC}$$

where **A** is known as the constant matrix; **K** is the coefficient matrix; and **C** is the variable matrix.

The concentrations of the unknowns in the variable matrix can then be determined from the following formula.

$$\mathbf{C} = \mathbf{K}^{-1}\mathbf{A}$$

Before the development of computers, the calculation of the obtained system of linear equations was very tedious, and several approximations were required.

Mathcad's notation is the same as that already presented. All one needs to know is how to enter the proportionality coefficients in one matrix and the absorbances in another (Fig. 4).

If a mixture of standards is used to account for the interactions between the molecules, then the matrices **A** and **C** are not necessarily square. In this so-called over-

[1]An excellent software package is STATGRAPHICS from Statistical Graphics.

Relative Intensities

m/z	A	B	C	Unknown mixture
15	56.42	15.23	1.89	39.16
26	2.53	1.98	61.08	33.72
27	9.27	4.53	61.95	39.05
29	0.25	2.05	0	0.10
31	21.52	0	12.87	18.62
44	15.41	16.72	32.51	32.72
45	70.05	28.01	73.11	89.05
46	47.63	8.37	100.00	81.72
47	21.45	2.95	4.05	15.35
58	15.27	6.45	0	11.37
72	68.95	51.21	0	61.10
73	100.00	100.00	0	100.00

The sensitivity of each component is defined in another vector row.

$$\mathbf{S} \equiv (0.240 \quad 0.422 \quad 0.160) \qquad \mathbf{i} \equiv 0 \cdots \text{last}\left[\mathbf{S}^{\mathrm{T}}\right]$$

The product of the partial pressure and the sensitivity is obtained from the following.

$$\mathbf{SP} \equiv \left[\mathbf{K}^{\mathrm{T}} \cdot \mathbf{K}\right]^{-1} \cdot \mathbf{K}^{\mathrm{T}} \cdot \mathbf{A} \qquad \mathbf{SP} = \begin{bmatrix} 0.558 \\ 0.442 \\ 0.514 \end{bmatrix}$$

The partial pressure is caluclated by dividing by the sensitivity.

$$P_i \equiv \frac{SP_i}{\left[\mathbf{S}^{\mathrm{T}}\right]_i} \qquad \mathbf{P} = \begin{bmatrix} 2.325 \\ 1.047 \\ 3.215 \end{bmatrix}$$

Finally the mole percent is calculated.

$$x_i \equiv \frac{P_i}{\sum_i P_i} \qquad \mathbf{x} = \begin{bmatrix} 35.3 \\ 15.9 \\ 48.8 \end{bmatrix} \%$$

Figure 5. Mathcad's input/output for the mass-spectroscopic analysis of a tricomponent mixture.

determined case, in which more standard mixtures are used than components, the concentrations are obtained from the following formula.

$$\mathbf{C} = (\mathbf{K}^{\mathrm{T}}\mathbf{K})^{-1}\mathbf{K}^{\mathrm{T}}\mathbf{A}$$

The usefulness of this formula can be illustrated in the mass-spectrographic analysis of multicomponent systems. The relative intensities are measured at different sensitivities for each component, when the number of fragments is usually greater than the number of components measured (Fig. 5).

Linear Regression

Statistics is gaining an ever increasing importance in all areas of science. There are several statistical packages designed for specific applications, as well as others that are for more general purposes.[1] All are very valuable. Once again, Mathcad is one of the better choices both for teaching and for applications that require full control of all calculations without the programming repercussions.

Concentration of sucrose

$$\mathbf{S} \equiv \begin{bmatrix} 0.0292 \\ 0.0584 \\ 0.0876 \\ 0.1170 \\ 0.1460 \\ 0.1750 \\ 0.2340 \end{bmatrix}$$

Initial rate

$$\mathbf{v} \equiv \begin{bmatrix} 0.182 \\ 0.265 \\ 0.311 \\ 0.330 \\ 0.349 \\ 0.372 \\ 0.371 \end{bmatrix}$$

$\mathbf{i} = 0 \cdots \text{last}(S)$

Dixon's equation: $\frac{S}{v} \equiv \frac{K_M}{V} + \frac{1}{V} S_n \qquad y_i \equiv \frac{S_i}{v_i}$

corr $(S, y) = 0.99864$ $a \equiv$ slope (S, y) $b \equiv$ intercept (S, y)

$V \equiv \frac{1}{a}$ $V = 0.44$ $K_M \equiv bV$ $K_M = 0.038$

The obtained values are entered in the Michaelis–Menton equation.

$$vt_i \equiv V\left[\frac{S_i}{S_i + K_M}\right]$$

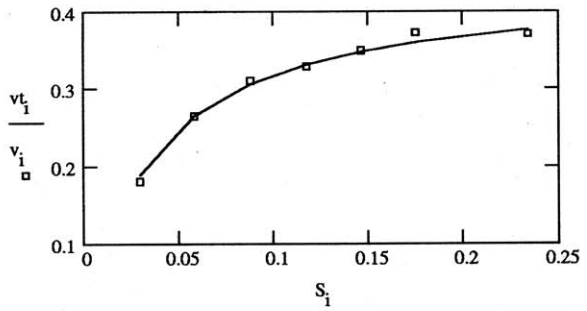


Figure 6. Regression analysis of enzyme activity.

Vector manipulation is essential in regression analysis. In the simplest case, two vectors are defined: one for the independent variable and one for the dependent variable. The linear correlation coefficient, the slope, and the intercept are all built-in statistical functions in Mathcad and are easily computed. It is well-known that polynomial and exponential functions can also be put in linear form using natural logarithms.

Other functions can also be transformed into linear form. For example, in biochemistry the activity of enzymes is often evaluated by the Michaelis–Menten equation below.

$$v = \frac{-\mathrm{d[S]}}{\mathrm{d}t} = k\,[\mathrm{ES}] = \frac{k\,[\mathrm{E}][\mathrm{S}]}{K_M + [\mathrm{S}]}$$

In practice this equation is often put in linear form, as shown below (*11*).

Lineweaver–Burk

$$\frac{1}{v} = \frac{K_M}{V[\mathrm{S}]} + \frac{1}{V}$$

Eadie

$$v = -\frac{v}{[\mathrm{S}]} K_M + V$$

Dixon

$$\frac{[\mathrm{S}]}{v} = \frac{K_M}{V} = \frac{1}{V}[\mathrm{S}]$$

where v is the rate; [S] is the concentration of the substrate; V is the maximum rate; and K_M is the Michaelis constant.

To find the linear correlation two vectors are defined: one for the initial rate, and another for the concentration of the substrate. In the Dixon equation, the correlation is between the concentration of the substrate and a new quantity defined as the ratio of the concentration and the initial rate (Fig. 6). These equations are very helpful, especially when used with Mathcad's plotting ability, for teaching the linear transformations and how they are accomplished.

Conclusion

The previous examples demonstrate the universal applicability of Mathcad for many of the array operations encountered in chemistry problems. More important, as can be seen from the figures, when printing the document, the output can be easily understood even without prior knowledge of Mathcad. We strongly feel that this is an excellent way to teach some very important calculations in chemistry.

The latest Windows version enables editing of documents using icons—further simplifying the use of Mathcad. Unfortunately, working with Windows is inexcusably slow. I highly recommend a computer that is more powerful than an AT and has a numerical coprocessor and much RAM.

Literature Cited

1. Coleman, W. F. *J. Chem. Educ.* **1990**, *67*, A203.
2. Zdravkovski, Z. *J. Chem. Educ.* **1991**, *68*, A95.
3. Rioux, F. *J. Chem. Educ.*: Soft. **1990**, *IIIB*, no. 2.
4. Knudson, S. K. *J. Chem. Educ.* **1991**, *68*, A39.
5. Rioux, F. *J. Chem. Educ.* **1991**, *68*, A282.
6. Rioux, F. *Am. J. Phys.* **1991**, *59*, 474.
7. Bolemon, J. S. *Am. J. Phys.* **1972**, 40, 1511.
8. Linnett, J. W. *Wave Mechanics and Valency*; Methuen: London, 1960; pp 89–91.
9. Robiette, A. G. *J. Chem. Educ.* **1976**, *52*, 95.
10. Zdravkovski, Z. *J. Chem. Ed.* **1991**, *68*(4), A95.
11. Moore, W. J. *Physical Chemistry*, 4th ed.; Prentice–Hall: Englewood Cliffs, NJ, 1972; p 410.