

the computer bulletin board

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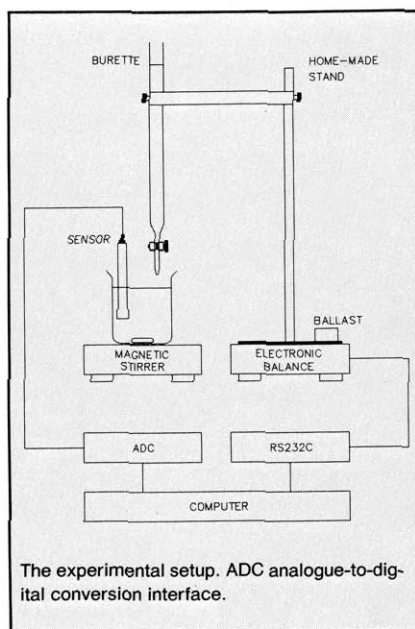
Microcomputer Automation of Volumetric Titration

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We report the microcomputer automation of volumetric titration using a standard, Teflon-stoppered, buret. The volume of the titrant is determined by the weight loss of the buret divided by the titrant density.

Most autotitrators use either a metering valve or a motorized syringe (1-4). Such a device is not only expensive but also may not be corrosion resistant to all titrants a chemist would put into a standard buret. There have also been reports of titration automation by measuring the weight loss of a titrant reservoir (5-7). One of these reports (7) also proposed measuring the weight gain of the titration beaker, but in this case a magnetic stirrer could not be used.



The experimental setup is shown in the figure. The sensor can be a glass electrode, ion selective electrode, colorimetric detector, indicator electrode, etc. The analogue-to-digital (ADC) interface includes a front end specific for the sensor. For example, if the sensor is a glass electrode, the front end will be an impedance-matching pre-amplifier made up of a CA3130² operational amplifier. The ADC data acquisition system has been described elsewhere (8).

The electronic balance is an Ohaus Galaxy 4000D that includes an RS232C inter-

face. This balance provides a weight resolution of 0.01 g if the total weight does not exceed 400 g. The total weight of the buret, titrant, stand, and ballast falls within this limit.

The main program starts by asking the operator either to enter the density value of the titrant or to determine the value immediately by taking a buret reading, running some titrant, and taking a second buret reading, while the program monitors the balance reading. The titration is started manually. Sensor reading is taken at 20 Hz in the background, while weight reading is taken as often as the BASIC program can manage, typically at a few hertz. Data are plotted on the screen and the endpoint is determined automatically from accumulated data; a change from a positive value to a negative value of the second derivative is taken as the endpoint. The titration is stopped manually after the endpoint has been determined; no attempt is made to stop the titration at the endpoint.

This automation is suitable for the IBM PC/XT/AT family (including clones) with a minimum of 256K memory and requires the ADC interface hardware and software described in ref 8, or equivalent. Most users would be able to write their own data processing software in a high level language, but a 5¼-in. disk containing AUTOTITR.BAT, IRQ.EXE, INITIAL.EXE, and MAIN-PROG.BAS can be obtained from the second author at a cost of US\$5 including airmail postage. Checks in US\$, Can\$, UK£, or HK\$ can be accepted.

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² A common component manufactured by Motorola and available from many suppliers.

Using MathCAD in Chemistry Calculations

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Computer software packages that allow numerical calculations, data manipulation, and graphic presentations are becoming invaluable in teaching and precious tools for practicing chemists and engineers. Just as the development of the scientific calculator in the '70's made all arithmetic less unattractive, the new mathematically inclined computer programs handle most computational chores gracefully, allowing one to concentrate on the problem itself. Another benefit is that, without much additional effort,

they expand the scope of problems that can be solved.

Examples for the use of such a program, Borland's Eureka, have appeared in this *Journal* (9, 10). In this article a few typical examples using another, even more powerful package, Math Soft's MathCAD¹, are presented (11). What makes this program so attractive is the excellent user interface that turns complicated calculations into formulas written naturally into two dimensions. Debugging such formulas is like checking your notes, unlike finding the syntax errors in FORTRAN, C, etc. Also, the results of such computations are just as natural as entering the formulas, and functions can easily be plotted.

These were the main considerations to use MathCAD as an example of "mathematical" software in a third-year computer chemistry course. The students have had enough general, physical, and analytical chemistry so they are able to solve, graph, and view some problems they had taken for granted in other courses. In a typical class we give the syntax for a command, illustrate it with an example, and then set a problem for the students to solve. The majority of students found the course very stimulating and provocative.

Plots

MathCAD plots are easy to create and very flexible. The size, type, grid, etc., can very easily be defined with simple, logical commands. An elementary example of plotting can be demonstrated with the isotherms obtained from the equation for ideal as well as the different real gas equations. The pressure is defined as a function of the volume and temperature. Either or both the volume and temperature can be defined as arrays. When using, for example, the van der Waals equation the constants a and b can be given in a separate file and the values for the desired gas simply recalled. Varying the volume and temperature, the plot can be used to estimate the conditions at which a given substance behaves as an ideal gas, thus giving the students a feeling about the limits of the ideal gas law.

Solving Cubic and Higher Order Equations

Cubic and higher order equations have been avoided in the calculator era, but now they can be solved just like linear or quadratic equations. A nice example is solving for the volume in the van der Waals equation for gases, a cubic equation.

It is advisable to estimate the volume first according to the ideal gas law and then to use that value as an initialization for the cubic expression. This way the complex roots are avoided, and the computation is

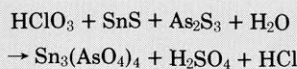
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speeded up. The cubic expression is solved using the *Root* function in MathCAD, although the *Given* and *Find* functions can be used as well.

Higher order equations are obtained in solving some equilibrium problems, such as the equilibrium concentrations of the components in the synthesis of ammonia from hydrogen and nitrogen, etc. One should always be aware of the number of possible mathematical roots to the expression and that only one is acceptable. This can be a problem sometimes since MathCAD uses the secant method, so a good practice is to graph the function first, and then from the graph determine a reasonable initialization value for the iteration.

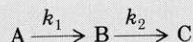
The *Given* and *Find* commands, used to solve a set or block of linear equations, can come in handy balancing some rather complicated reactions such as:



Students find these examples rather amusing since they seem to forget that the chemical equations are also mathematical expressions, so the computer can balance them even without any knowledge of oxidation states, electron transfer, etc.

Differential Equations

An example of radioactive decay is included in the MathCAD computer package. It can be changed somewhat, so that the reactions take place according to the following scheme:



The solutions to the different equations are discussed in physical chemistry courses and can be easily entered into MathCAD for each component. The three curves of the concentrations of each component with time can be graphed on one plot, an advantage over Borland's *Eureka*, which can display only one curve at a time. The time when the maximum concentration of B is reached, and the concentrations of each component at a given time, can easily be computed. By varying the values of the constants k_1 and k_2 different plots can be obtained and discussed.

An attractive feature given in the advanced math pack is the example of solving a system of differential equations. A numerical solution for a system of two first-order equations is reached by a fourth-order Runge-Kutta algorithm. This example can readily be adapted to our consecutive reactions example by introducing the differential equations for dA/dt in $F(t,A,B)$ and dB/dt in $G(t,A,B)$. The rate constants need to be defined, as well as the initial concentrations of A and B and the starting and ending times. The concentration of the third component, the end product C, given by the expression

$$c(C) = c_0(A) + c_0(B) - (c(A) + c(B)),$$

can be included so the plot can be completely comparable to the previous example.

Derivatives

Titration curves are important in the understanding of a number of analytical methods. Basically they are all very similar: the change in a physical property is calculated as new portions of titrant are added.

For example, in acid-base titrations the concentration of the hydrogen ion has to be computed by at least three expressions: up to the equivalence point, at the equivalence point and after the equivalence point. The calculation of the pH values at, e.g., 10 points, can be both time consuming and boring.

This kind of problem can be handled in MathCAD using the conditional *if* expression. Once the equations have been written the initial conditions can easily be changed such as the volume increments of the titrant, concentrations, or the acid or base constants. The plot of the curve can be used for a discussion of the most adequate indicator for a reaction.

Defining the first derivative of a function in MathCAD is remarkably easy. The first derivative of the titration curve function, and its plot is a nice illustration of the differential analytical methods.

Similar equations can be introduced for plotting other titration techniques such as potentiometric, redox, etc.

Conclusion

These examples illustrate just a few of the possibilities of MathCAD in simplifying some more demanding problems in chemistry. *Calculations with matrices* can also be done with Version 2. The program has also some statistical functions, although specialized statistical packages are probably more powerful.

Students with practically no prior computer experience (even with no knowledge of English, all commands and help menus are in English) master such calculations, with immense pleasure, in a matter of hours. If an overhead projection monitor is available, the program can be used to enhance lecture presentations whenever calculations are involved.

The hardware requirements for the program are standard, 512 K RAM, with practically all graphic cards, a great number of printers and plotters and mathematical coprocessors being supported. The "MathCAD" files presented here can be obtained by sending a preformatted disk to the author.

¹ MathCAD by MathSoft Inc., One Kendall Square, Cambridge, MA 02139.

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