

- (26) Jacobus, D. P.; Davidson, D. E.; Feldman, A. P.; Schafer, J. A. "Experience with the Mechanized Chemical and Biological Information Retrieval System". *J. Chem. Doc.* 1970, 10, 135-140.
- (27) Meyer, E. "The IDC System for Chemical Documentation". *J. Chem. Doc.* 1969, 9, 109-113.
- (28) Dammers, H. F.; Polton, D. J. "Use of the IUPAC Notation in Computer Processing of Information on Chemical Structures". *J. Chem. Doc.* 1968, 8, 150-160.
- (29) Skolnik, H. "A Chemical Fragment Notation Index". *J. Chem. Doc.* 1971, 11, 142-147.
- (30) Bowman, C. M.; Landee, F. A.; Lee, N. W.; Reslock, M. H.; Smith, B. P. "A Chemically-Oriented Information Storage and Retrieval System. III. Searching a Wiswesser Line Notation File". *J. Chem. Doc.* 1970, 10, 50-54.
- (31) Eakin, D. R.; Hyde, E. "Evaluation of Online Techniques in a Substructure Search System". In "Computer Representation and Manipulation of Chemical Information"; Wipke, W. T.; Heller, S. R.; Feldmann, R. J.; Hyde, E., Eds.; Wiley: New York, 1974; pp 1-30.
- (32) Crowe, J. E.; Leggate, P.; Rossiter, B. N.; Rowland, J. F. B. "The Searching of Wiswesser Line Notations by Means of a Character-Matching Serial Search". *J. Chem. Doc.* 1973, 13, 85-92.
- (33) Garfield, E.; Revesz, G. S.; Granito, C. E.; Dorr, H. A.; Calderon, M. M.; Warner, A. "Index Chemicus Registry System: Pragmatic Approach to Substructure Chemical Retrieval". *J. Chem. Doc.* 1970, 10, 54-58.
- (34) Thomson, L. H.; Hyde, E.; Matthews, F. W. "Organic Search and Display Using a Connectivity Matrix Derived from Wiswesser Notation". *J. Chem. Doc.* 1967, 7, 204-209.
- (35) Granito, C. E.; Rosenberg, M. D. "Chemical Substructure Index (CSI)—A New Research Tool". *J. Chem. Doc.* 1971, 4, 251-257.
- (36) Richman, S.; Hazard, G. F., Jr.; Kalikow, A. K. "The Drug Research and Development Chemical Information System of NCI's Developmental Therapeutics Program". *ACS Symp. Ser.* 1978, No. 84, 200-221.
- (37) Schenk, H. R.; Wegmuller, F. "Substructure Search by Means of the Chemical Abstracts Service Chemical Registry II System". *J. Chem. Inf. Comput. Sci.* 1976, 16, 153-161.
- (38) Graf, W.; Kaindl, H. K.; Kniess, H.; Schmidt, B.; Warszawski, R. "Substructure Retrieval by Means of the BASIC Fragment Search Dictionary Based on the Chemical Abstracts Service Chemical Registry III System". *J. Chem. Inf. Comput. Sci.* 1979, 19, 51-55.
- (39) Graf, W.; Kaindl, H. K.; Kniess, H.; Warszawski, R. "The Third BASIC Fragment Dictionary". *J. Chem. Inf. Comput. Sci.* 1982, 22, 177-181.
- (40) Fisanick, W.; Mitchell, L. D.; Scott, J. A.; Vander Stouw, G. G. "Substructure Searching of Computer-Readable Chemical Abstracts Service Ninth Collective Index Chemical Nomenclature Files". *J. Chem. Inf. Comput. Sci.* 1975, 15, 73-84.
- (41) Dunn, R. G.; Fisanick, W.; Zamora, A. "A Chemical Substructure Search System Based on Chemical Abstracts Index Nomenclature". *J. Chem. Inf. Comput. Sci.* 1977, 17, 212-219.
- (42) Blake, J. E.; Brown, S. M.; Ebe, T.; Goodson, A. L.; Skevington, J. H.; Watson, C. E. "Parent Compound Handbook—Successor to The Ring Index". *J. Chem. Inf. Comput. Sci.* 1980, 20, 162-167.
- (43) Farmer, N. A. "The Proposed Chemical Abstracts Service's Substructure Search System". In "Proceedings of the Technical Information Retrieval Committee of the Manufacturing Chemists Association", Arlington, VA, Aug 1977; McNulty, P. J.; Smith, R. B., Eds.; Manufacturing Chemists Association: Washington, DC, 1977.
- (44) Zeidner, C. R.; Amoss, J. O.; Haines, R. C. "The CAS ONLINE Architecture for Substructure Searching". In "Proceedings of the National Online Meeting, 3rd"; Learned Information Inc.: Medford, NJ, 1982; pp 575-586.
- (45) Attias, R. "DARC Substructure Search System: A New Approach to Chemical Information". *J. Chem. Inf. Comput. Sci.* 1983, 23, 102-108.
- (46) Feldmann, R. J.; Milne, G. W. A.; Heller, S. R.; Fein, A. E.; Miller, J. A.; Koch, B. "An Interactive Substructure Search System". *J. Chem. Inf. Comput. Sci.* 1977, 17, 157-163.
- (47) Milne, G. W. A.; Heller, S. R.; Fein, A. E.; Frees, E. F.; Marquart, R. G.; McGill, J. A.; Miller, J. A.; Spiers, D. S. "The NIH-EPA Structure and Nomenclature Search System". *J. Chem. Inf. Comput. Sci.* 1978, 18, 181-186.
- (48) Feldmann, R. J.; Heller, S. R. "An Application of Interactive Graphics—The Nested Retrieval of Chemical Structures". *J. Chem. Doc.* 1972, 12, 48-54.
- (49) Tomea, A. V.; Sorter, P. F. "Online Substructure Searching Utilizing Wiswesser Line Notations". *J. Chem. Inf. Comput. Sci.* 1976, 16, 223-227.
- (50) Sarkisian, J. "Introduction to ISI's New Online Chemical Information Services—An Integrated Search System for Chemical Information"; 188th ACS National Meeting, Philadelphia, PA, Aug 31, 1984; American Chemical Society: Washington, DC, 1984.
- (51) Brown, H. D. "Substructure Searching of Chemical Files". In "Proceedings of the Technical Information Retrieval Committee of the Manufacturing Chemists Association", Arlington, VA, Aug 1977; McNulty, P. J.; Smith, R. B., Eds.; Manufacturing Chemists Association: Washington, DC, 1977.
- (52) Bond, V. L.; Bowman, C. M.; Davison, L. C.; Roush, P. F.; McGrew, R. D.; Williams, D. G. "Online Storage and Retrieval of Chemical Information. II. Substructure and Biological Activity Searching". *J. Chem. Inf. Comput. Sci.* 1979, 19, 231-234.
- (53) Wipke, W. T.; Dyott, T. M. "Stereochemistry Unique Naming Algorithm". *J. Am. Chem. Soc.* 1974, 96, 4834-4842.
- (54) Kaback, S. M. "Chemical Structure Searching in Derwent's World Patents Index". *J. Chem. Inf. Comput. Sci.* 1980, 20, 1-6.

## Digital Computers in Electrochemistry

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The history and current status of digital computing in electrochemistry are reviewed. Six different roles are distinguished: (a) sample preparation, (b) experimental control, (c) preparation of data for interpretation, (d) model building, (e) interpretation, and (f) tactical and strategic decision making. Due to the small amount of work in area a, it is not discussed in detail. Each of the remaining five areas is discussed separately.

### INTRODUCTION

The advent of computing equipment has had a massive impact on almost every aspect of scientific life over the past quarter century, and electrochemistry has shared in those changes. In fact, the effects on electrochemistry predate those in most other areas of chemistry for interesting reasons. The modern era began in the middle 1950s, when potentiostats and function generators based on operational amplifiers were first invented. They gave electrochemists access to a much wider range of wave forms with which to excite an electrochemical system, and they introduced much shorter time scales than had previously been investigated with any seriousness. The new instrumentation made possible the very extensive devel-

opment of new electrochemical methods that took place throughout the 1960s. Since operational amplifiers were themselves invented for analog computing, one can say entirely accurately that the advent of computing equipment gave birth to modern electrochemistry and has driven its development for 30 years.

Of course, the intent of this issue is to celebrate the improvements wrought by digital computing, not analog computing, on chemistry. Aside from this little reminder about deep roots, we will be true to that theme. Digital computing has had the most sophisticated of influences on electrochemistry: It has changed the way electrochemists think about doing electrochemistry, and it has widened the spectrum of



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scientists interested in doing electrochemistry. Here, we hope to highlight the way in which those influences were established, and we want to provide a glimpse of future prospects. It is, of course, impossible for us to cite all examples of valuable contributions in which computing has played a part.

One can discern six different roles for digital computers in electrochemistry, viz., (a) sample preparation, (b) experimental control, (c) preparation of data for interpretation, (d) model building, (e) interpretation, and (f) tactical and strategic decision making. Electrochemistry has seen rather little use of computers in sample preparation, but there have been extensive applications in the control of experiments, in the treatment of data prior to interpretation, and in the construction of theoretical models. In defining the fifth role, interpretation, we address the situation in which a computer draws a major chemical conclusion from an invariant body of data. Such a conclusion might be quantitative, e.g., the  $n$  value of an electrode reaction, or it might be qualitative, e.g., a diagnosis of mechanism. In this sphere, there has been

significant, although not widespread, research. The final role is the most sophisticated one. It covers situations in which a computer can draw conclusions in an interpretative fashion and then act on those conclusions to get additional data, perhaps by requesting additional experiments, until it is satisfied with the quality of its overall conclusions. In this capacity, the computer serves as an active project planner and director, not merely an experimental supervisor or an interpreter of invariant data. There has been rather little work in this area in any context, but the research that has been done in electrochemistry is exciting and promising.

The remainder of this paper is organized by these roles. Since there has been so little work in automated sample preparation, that role will not be discussed further. The remaining five will be taken in the order given above.

## EXPERIMENTAL CONTROL

When experimental chemists consider the influence of computers in their world, the aspect that springs most quickly to mind is the direct supervision and optimization of measurements. This is the domain in which the computer perceives and acts upon the world via its interfaces with sensors and control devices. Developments in this area have filled many pages of the literature of the last 25 years. Even restricting our view to electrochemistry, we could not review them in detail; hence, we will try only to trace the main lines of development and offer a prognosis.

The business end of almost any instrument used for faradaic electrochemistry, regardless of how thoroughly supervised by a computer it might be, is still an analog potentiostat, and the quantities of interest are all members of the analog domain, viz., current or charge, time or frequency, and potential. Interfacing is quite straightforward. The central processor imposes its will via DAC's, senses electrical variables via ADC's, controls switches via digital lines, and sequences operations with clocks. Most experiments are carried out on time scales of a few milliseconds or longer, and the operations are easily handled by a single computer. In electrochemistry, very fast experiments are only in the microsecond range, and these can still be handled under computer control with careful selection of components.

On-line control of electrochemical experiments began in the middle 1960s, and it is satisfying to realize now that the first developments were driven by necessity, rather than novelty. Anson had just invented the technique of chronocoulometry and had shown that it would be a powerful, general tool for elucidating interfacial structure.<sup>1</sup> Its drawbacks were serious for the time: The measurements had to be carried out on a time scale of a few hundred milliseconds; analysis of results required construction of straight line plots of electrolytic charge vs. square root of time variables, and many experiments were needed to characterize any given chemical system. In the conventional practice of the time, the charge-time transients would be recorded on an oscilloscope, from which they would be photographed. Individual data points would be taken by hand from the photographs, and the linear plots would be constructed. The tedium of the procedure was amplified by the number of times that it had to be repeated. Lauer et al. recognized that the drawbacks presented no difficulty to a computer-based data acquisition system, and they reported such a system in 1967.<sup>2</sup> Their equipment introduced electrochemists to the improved precision that usually comes about in computer-controlled experiments as a consequence of superior means for digitization of analog variables and a fuller utilization of the data in calculating a result. Even now, chronocoulometry is an excellent example of a powerful electrochemical technique that is not practical without a computer.

Computer-based electrochemical instruments have many general advantages over traditional designs.<sup>3</sup> First, they are extremely flexible. With the basic analog circuitry and proper interfacing, many different operations can be accomplished by software without alterations to the hardware design. This feature is particularly important for multifunctional instruments, and it makes the modification and updating of any system much more convenient and cheaper. Second, the high speed of the computer makes a wide range of time scales more conveniently accessible. Third, the acquired data can be stored for various forms of display and processing. These operations can occur nondestructively and at leisure. Finally, intelligent control is also possible. By monitoring a system's responses to the controlled parameters, the computer can make adjustments toward optimal control.

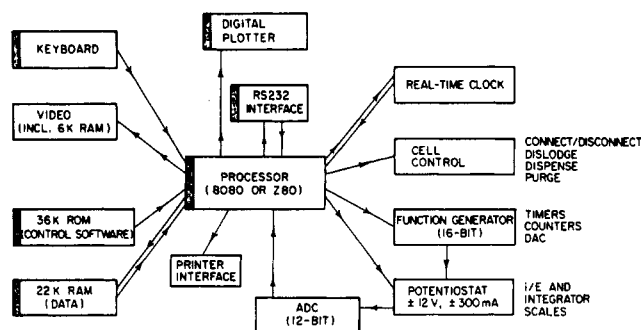
Lauer and Osteryoung were first to recognize these advantages in an electrochemical context, and they generalized their initial chronocoulometric system to produce a more flexible laboratory data acquisition and control system.<sup>4</sup> The two Osteryoungs then extended that basic idea to create a very flexible computer-based system tailored to the needs of pulse voltammetry.<sup>5,6</sup> Over the past dozen years they have experimented with the effects of a great variety of excitation wave forms, and they have developed pulse voltammetry to a high level of scientific understanding. The contemporary practice of these techniques, which include normal-pulse, differential-pulse, reverse-pulse, and Osteryoung square wave voltammetries, places high value on an ability to use wide variations in pulse frequencies and wave-form shapes.<sup>6</sup> The power of these methods has been revealed because they were developed with computer-based instrumentation, and bringing that power to bear fully on any chemical system is not possible outside of computer control.

Probably the most sophisticated computer-controlled electrochemical instrument is the Fourier-transform faradaic admittance equipment developed by Smith and his co-workers.<sup>7</sup> The whole strategy is made possible by pre- and postmeasurement transformations of data, so we reserve discussion of it for the next section.

In the early stage of computer applications in electrochemistry, minicomputers dominated. As the cost and size of computers have declined dramatically during the last 10 years, microcomputers have found an indisputable position in experimental control. Interfacing and data domain conversion once were art; now they turn out to be simple technology. The well-established general methodology of hardware and interfacing has lead to general applications of computers in electrochemical instrumentation.

Anderson and Bond taught an important lesson via microcomputer-based equipment in which important signal processing functions needed for ac voltammetry were handled by software.<sup>8</sup> First, the ac perturbation was software generated. To generate the signal and acquire data at a reasonable speed, a look-up sine table was used to supply the stream of control values that were applied to the DAC driving the potentiostat. The function generation and data acquisition for ac, phase-selective ac, and second-harmonic ac techniques were all the same. The methods differed only in the data processing used. For this purpose, a software ac coupler and absolute value amplifier, a software lock-in amplifier, and a software-tuned amplifier were developed. These functions, which used to be allotted to analog circuitry, were mimicked simply and precisely by software.

Over the years, electrochemists have armed themselves with a host of different techniques for characterizing chemical systems. The methods tend to be useful in different ways. Some are well suited to analysis, others to characterization of electrode processes. Even within the diagnostic group, for



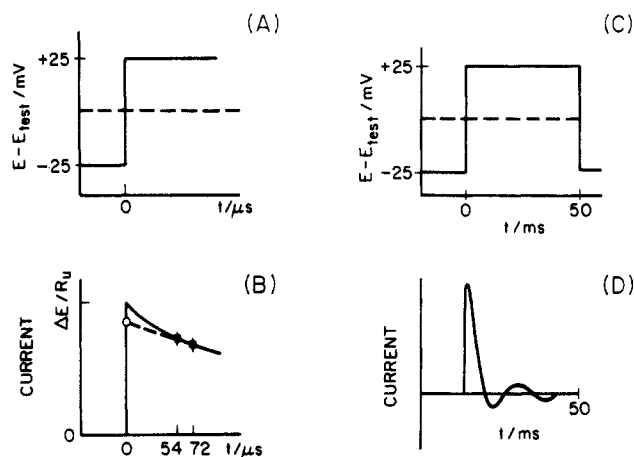
**Figure 1.** Block diagram of the cybernetic potentiostat described in reference 10. The repertoire includes essentially all kinds of voltammetry that can be implemented at single microelectrodes, plus bulk electrolysis, measurements of electrocapillary curves, and chronocoulometry. Voltammetric sweep rates between  $1 \mu\text{V/s}$  and  $50 \text{ V/s}$  can be applied. The instrument services the PARC Model 303 SMDE.

example, there are also special roles for certain techniques: chronocoulometry for examining adsorption, bulk electrolysis for measuring  $n$  value, and cyclic or Osteryoung square wave voltammetry for defining product stability. Effective electrochemical investigation requires access to a repertoire, yet commercial equipment available before 1983 did not offer that access.

In 1982, we addressed this problem by developing a cybernetic potentiostat, in which all interactions between the operator and the cell were mediated by a microprocessor.<sup>9,10</sup> A block diagram is shown in Figure 1. The processor controlled (a) switching of the cell, (b) coordination of mechanical functions (such as drop dislodgement and stirring), (c) synthesis of all wave forms applied to the cell, (d) acquisition of data, (e) display and plotting of results, and (f) extraction of more important results (e.g., Anson slopes and intercepts or peak potentials and peak heights). About 30 different methods could be implemented via keyboard commands, and experimental parameters could be set with full flexibility.

The cybernetic potentiostat has provided a very clear example of the way in which ready access to a repertoire can change the style of doing science. This instrument can easily perform 30–50 experiments in an hour, and it offers complete freedom to vary technique. One literally begins to play *études chimiques* at the keyboard. In facing a new chemical system, there is no need to record anything at the outset. One simply orders a first experiment and watches the result on the video display. This experiment suggests others, and within the span of 1 h, one will have probed behavior of several different kinds of experiments covering a wide range of time scales. The salient features of behavior become quickly understood. Then, a few particularly pertinent experiments can be performed with an eye toward saving the results in permanent form. One advantage of this style is that it makes electrochemistry more fun. Another is that it enables the assembly of a comprehensive picture of behavior much more quickly than conventional styles of investigation will allow; hence, less time is spent in blind alleys. Finally, the use of several techniques reduces the stress on results from any particular method. Electrochemistry is notorious in offering not quite theoretical responses in real experiments. By employing several methods to examine a system, one reduces the chance that misassignments of behavior will be made from nonidealities in response. Our point here is that there is substance to the new style: The advent of the cybernetic potentiostat has made possible an improvement in the strategy of measurement.

Within the cybernetic potentiostat, we have also implemented a new approach to the compensation of cell resistance.<sup>10</sup> It is of interest because it is a rare example of an experimental procedure in which a computer uses results from



**Figure 2.** Scheme of automatic resistance compensation. (A) Step to measure uncompensated resistance.  $E_{\text{test}}$  is normally in the non-faradaic region. (B) Response to step in (A). Sampling procedure provides estimate of  $R_u$  by extrapolation to  $t = 0$ . (C) Step wave form used in stability test. (D) Response to wave form in (C). Undershoot develops as potentiostat approaches oscillation.

one set of measurements to guide its plan for subsequent measurements. Uncompensated resistance is a serious plague in electrochemical measurements because it undermines interpretation. In our view, a truly automatic means for reliable compensation is a prerequisite for the use of electrochemical equipment by nonelectrochemists on any serious scale, and our development was driven by that view. We felt that reliability required both a measurement of the uncompensated resistance before compensation was attempted and a means for guarding against oscillation of the potentiostat as full compensation was approached.

The successful method is outlined in Figure 2. First, the uncompensated resistance is measured by applying a 50-mV step in a non-faradaic region of the potential scale. Two samples of the decaying charging current are made, and the current at the leading edge of the step is made by back-extrapolation. From it the uncompensated resistance can be calculated. Then, the microcomputer uses a multiplying DAC to apply a positive feedback. This is done in stages, and at each stage the system tests itself for stability via additional 50 mV step experiments. As the oscillation point is approached, an undershoot develops in the current transient produced by the step, as shown in Figure 2D. When the degree of undershoot, relative to the initial peak current, reaches a threshold, the system takes action to stabilize the potentiostat and proceeds with additional increments of compensation. It will stop upon reaching either full compensation or a point where it cannot proceed without exceeding the undershoot threshold. Usually, full compensation can be achieved.

The future will probably bring more examples of intelligent optimization similar to this approach for compensation of resistance. It may also bring some instrument designs that are intrinsically digital. To date, there have been several attempts to develop potentiostat emulators based on computer-controlled charge packet injection, but these devices are still too slow to compete on common ground with analog equipment. They may yet prove valuable in systems with extraordinarily high resistance. In the near term, we may see a need for intrinsically digital methods of current measurements, because the rapidly increasing use of ultramicroelectrodes is pushing us toward a situation in which electron counting could be both feasible and desirable.

#### PREPARATION OF DATA FOR INTERPRETATION

It is often desirable to process experimental data before they are interpreted. Data may be smoothed, a background may

be corrected, overlapped peaks may be resolved, and peaks or waves may be quantified. These steps are important because they distill the useful information into a more compact, understandable form. On the other hand, they do not alter experimental strategy because they involve the same methods of data reduction that a trained electrochemist would use.

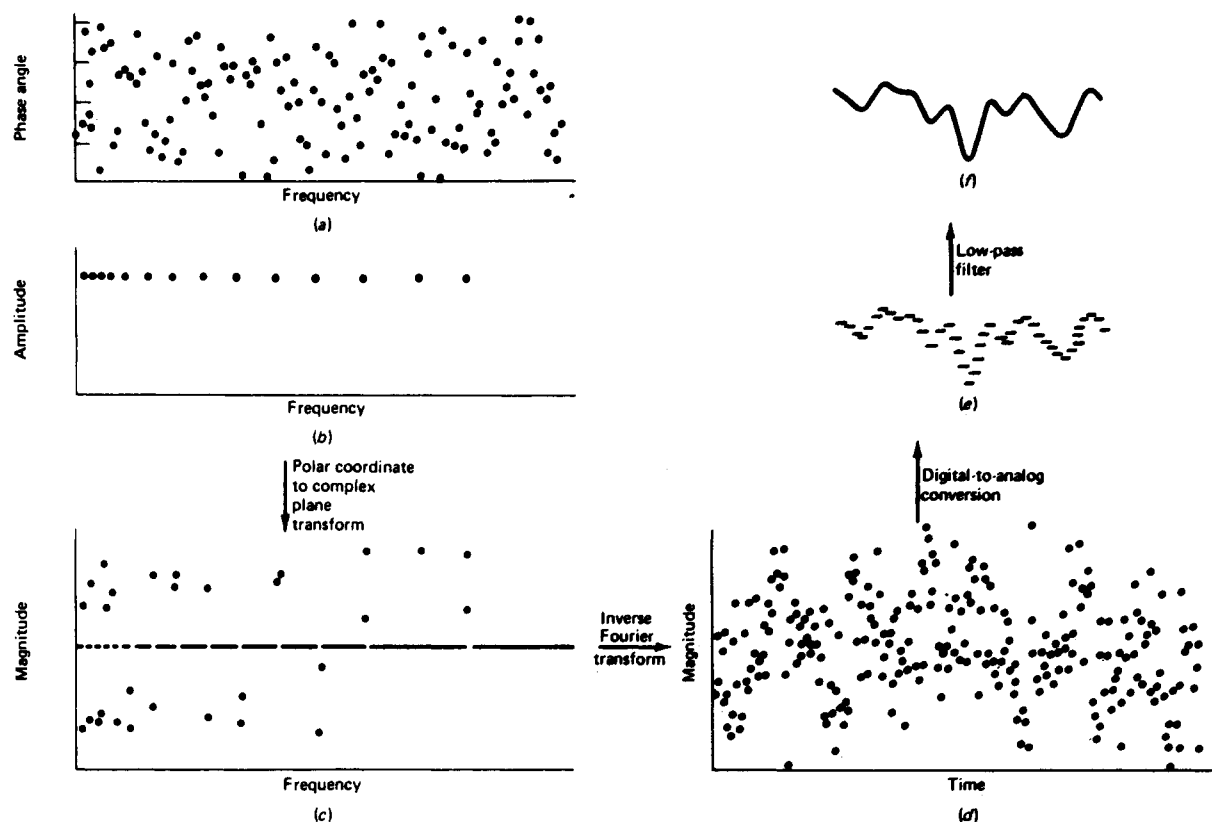
Other methods for handling data have a more fundamental impact. The applications of Fourier and Laplace transforms provide the best examples. If a time domain function,  $f(t)$ , is transformed, a new function,  $F(j\omega)$ , in the frequency domain, will be obtained. This feature is useful for electrochemists, since experimental data are normally measured in the time domain, but many parameters of interest are more easily extracted by analysis in the frequency domain.

The most impressive application of the Fourier transform (FT) in electrochemistry is in faradaic admittance measurements,<sup>11</sup> which are extremely useful in studies of electrode kinetics. The FT approach is fundamentally different from the classical ac impedance measurements (single potential, single frequency) and ac voltammetric measurements (automatic potential scan, single frequency). In FT-FAM, one applies a signal with several frequency components to the electrochemical cell while the potential is scanned. The procedure is illustrated in Figure 3. One chooses the frequency distribution and amplitude in the frequency domain, takes the inverse transform, and applies a synthesized time domain signal to the chemical system. Both the applied potential and the current response are recorded as functions of time, and both sets of data are then transformed back into the frequency domain. The different frequency components of the perturbation signal and response are immediately apparent. The transfer function, i.e., the frequency-dependent faradaic admittance, is then computed.

Standard heterogeneous rate constants up to 1 cm/s can be measured easily by the FT method.<sup>12</sup> To obtain a rate constant value of a given magnitude, the highest frequency needed in FT-FAM is approximately 3 orders of magnitude lower than that required in faradaic rectification or double-step galvanostatic techniques.<sup>13,14</sup>

Still another domain for computational methods is the improvement of the quality of data before interpretation. For example, the removal of noise without distortion of the signal can be extremely helpful. Common digital smoothing operations are effective, but they also introduce distortion. Better results can be obtained by Fourier-transform techniques.<sup>15</sup> Data to be smoothed are first transformed into the frequency domain. Since electrochemical data normally occupy a relatively low-frequency spectrum, whereas the noise distributes over a much wider band, the frequency spectrum of the raw data can be multiplied by a rectangular filter function, which passes the low-frequency components but cuts off the high-frequency ones. The smoothed time domain signal is recovered by the inverse Fourier transform. The results are correspond to ideal filtering; i.e., the response decays infinitely sharply at the cutoff frequency. Comparable results are very difficult to achieve in the time domain.

The Fourier transform can also be used to increase the density of a sparse data set.<sup>16</sup> First, a set of time domain data points is transformed. By filling zeros into the high-frequency portion of the Fourier spectrum, more points are added to the data set without altering the shape of the time domain signal. When the inverse transform is taken, more data points exist to define the time domain signal, and the data density is increased. O'Halloran and Smith showed that a voltammetric peak can be reconstructed from only 10 data points without apparent distortion.<sup>16</sup> This form of interpolation can be useful, because the use of a low density of acquired data permits a high scan rate and a short experiment completion time.



**Figure 3.** Synthesis of excitation wave form for FT-FAM. (a and b) Numeric-amplitude and phase-angle arrays for components of the proposed excitation signal. (c) Complex plane representation of arrays in (a) and (b). (d) Digital time domain representation of the arrays in (a) and (b) or in (c). (e) Analog representation of numbers in (d). (f) Filtered signal applied to cell. In measurement, these steps are applied to reverse to convert the actual excitation signal and the current responses back into phase and amplitude arrays. Reprinted with permission from Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980. Copyright 1980 John Wiley & Sons, Inc.

In multicomponent analysis, overlapping peaks often present a serious problem. To enhance the resolution, peaks can be sharpened by deconvolution. Numeric deconvolution in the time domain is very complex, but the Fourier transform allows a great simplification, since deconvolution can be done in the frequency domain by division. An example of peak sharpening is in Smith's work with overlapped ac voltammograms.<sup>17</sup> Two-electron peaks with 20-mV separation could be resolved.

Finally, the Fourier transform is useful in data compression. Since a voltammogram usually contains only low-frequency components, an entire voltammetric curve can be well represented by only a few Fourier coefficients. This property may prove useful in data storage and transmission.

Transformations aside from those based on Fourier integrals have also seen duty in an electrochemical context. Among the most interesting have been certain convolution procedures, which are also known as procedures for "fractional" differentiation or integration. They were brought into electrochemistry by Oldham and by Imbeaux and Saveant from separate directions.<sup>18</sup> Later, their work was understood to involve a common foundation. These transformations were originally introduced because they could remove the characteristic  $1/t^{1/2}$  dependences in current responses to potential steps and potential sweeps. Such a dependence arises from diffusion, and by removing it, one gains a clearer view of the other dynamics in a system. Soong and Maloy<sup>19</sup> have pointed out that related transformations of data can be used to remove any time dependence to a fractional power, and they have provided some interesting illustrations of the power of this idea via numeric analyses of current transients at a dropping mercury electrode. In the nomenclature of Soong and Maloy, data are subjected to a *Riemann-Liouville transform* (RLT) of order  $k$  to remove a time dependent of  $t^k$ . Saveant's term "convolution" and Oldham's "semiintegration" are synonyms

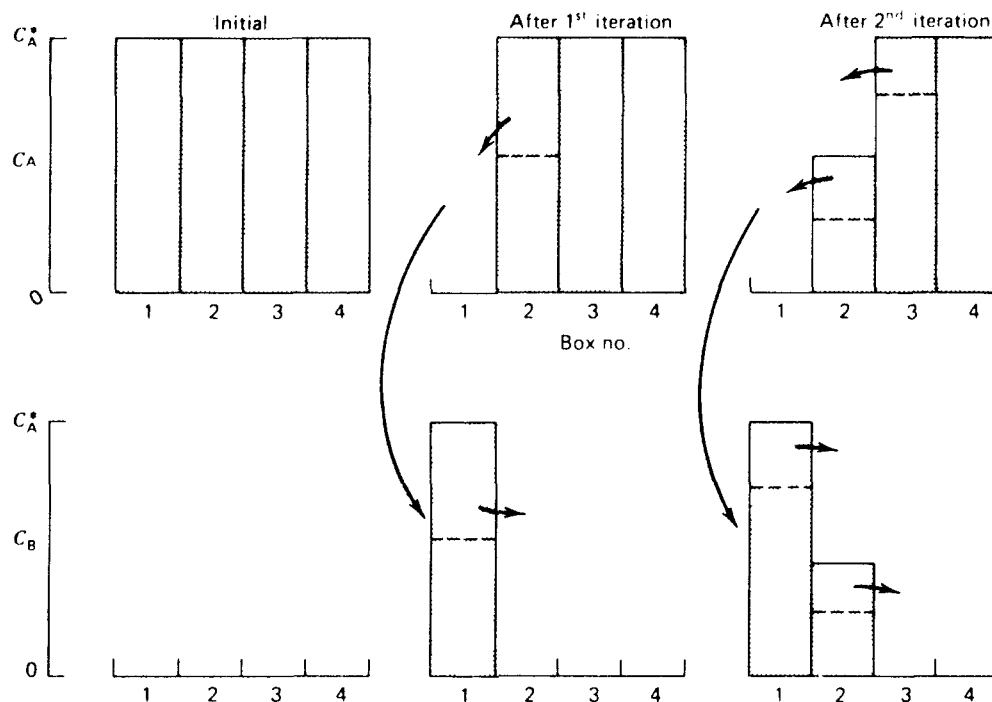
for the RLT of order  $-1/2$ . The small amount of work already in the literature suggests that RLT methods can be of genuine value in the simplification of results prior to interpretation. One can anticipate growth in their use.

## MODEL BUILDING

The prediction of electrochemical response functions for various perturbations of current or potential, or for various mechanisms, normally requires the solution of a set of coupled differential equations describing the diffusion and reaction of all species involved in the electrode process. For simple situations, an analytical solution might be reached. More generally, an analytical solution is inaccessible, and a numerical one must suffice. Computers play a general role in efforts along this line.

Of particular value have been the group of finite-difference modeling methods that provide *digital simulations* of electrode processes.<sup>20-22</sup> They were introduced to electrochemistry by Feldberg in the early 1960s,<sup>20</sup> and they have become very generally used. They are popular because they provide a detailed visualization of events in the diffusion layer and because they are readily adaptable to different experimental situations.

All of these methods involve quantized time and distance axes. That is, one develops a picture of the solution near an electrode as being divided into "boxes", each of definite width (e.g., a constant value  $\Delta x$ ) and containing uniform concentrations of all species. The array of boxes is characterized by arrays of concentrations that exist at some particular time. Because of diffusion and reaction kinetics, the arrays are not generally static. They evolve, and one calculates the state of the system (i.e., new arrays) for successive definite times, which are often equally spaced (e.g.,  $\Delta t$ ,  $2\Delta t$ ,  $3\Delta t$ , ...). The process



**Figure 4.** First three sets of arrays describing a system at  $t = 0$ ,  $\Delta t$ , and  $2\Delta t$  in a simulation. The electrode surface is in the middle of box 1. The conversion  $A \rightarrow B$  takes place at the electrode, and after  $t = 0$ , species A is not allowed to exist in box 1. In the initial situation, there is a uniform profile of A in the solution and there is no B. At  $t = \Delta t$  (the middle pair of arrays), A has been converted to B in box 1, but no material has diffused to or from more remote boxes. At  $t = 2\Delta t$ , some A has diffused into box 1 from box 2, where it has been converted into B. Some B has diffused from box 1 into box 2. The arrows show how the arrays for  $t = \Delta t$  are converted into those for  $t = 2\Delta t$  and how those for  $2\Delta t$  would change into new ones for  $3\Delta t$ . Reprinted with permission from Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980. Copyright 1980 John Wiley & Sons, Inc.

is shown in Figure 4 for the first two iterations of a simulation of the Cottrell experiment.

The heart of the concept is that differential equations can be turned into arithmetic ones by quantizing the axes of concern. Thus, the rules for transforming a set of arrays characterizing one time into the corresponding set for the next time are simple and are well adapted to a computer's capabilities. This is always true; hence, the method enables any set of diffusion-kinetic equations to be treated, regardless of the kinetic complexity and regardless of the applied electrochemical excitation function.

There is some trickiness to treating processes that occur on widely disparate spatial or time scales, and a good deal of the development that has gone into simulation methods recently has been aimed at this difficulty. It is not necessary for us to describe the various algorithmic strategies here.

Simulations are being applied to a larger and larger variety of problems. Some of them, such as the modeling of current responses at arrays of ultramicroelectrodes in flowing streams, are so complex that one could not imagine treatments other than by simulation. In other instances, an analytical solution might be possible, but simulation is used anyway because it is easier. The great strengths of simulation are its versatility and its ability to build a person's intuition about the distribution of events throughout the volume of a diffusion layer. Its drawbacks are those of almost all numeric modeling methods: It is difficult to be sure that a correct model has been constructed, and it can be hard to derive functional relationships that allow straightforward tests of a model.

Even with its drawbacks, use will continue to increase, because electrochemistry is addressing problems that, to a progressively larger degree, cannot be treated otherwise. A useful development would be the serious adoption of standard simulation packages, akin to the packages available for electronic structure calculations. They would improve one's confidence in the host of simulations reported casually in the literature, partly because of the quality of modeling would

probably improve (on the average) and partly because it would become much easier to reproduce and follow up a published report.

## INTERPRETATION

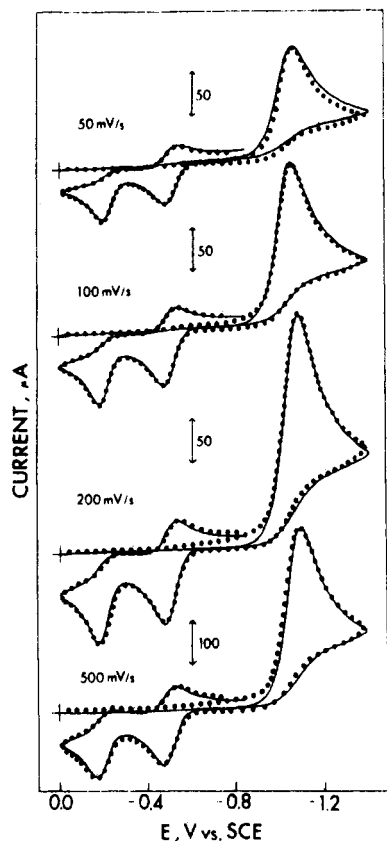
Interpretation of measurements to yield a conclusion always involves comparison with a model of behavior. Computing is playing an increasing role in such comparisons, often because the models are becoming more commonly numeric, rather than analytical.

In the interpretation of a set of data, such as a group of cyclic voltammograms for various scan rates, one might first be interested in establishing a mechanism, then in evaluating rate constants. One effective approach is to simulate expected voltammograms for a candidate mechanism for a spectrum of kinetic parameters. If the mechanism is consistent with the observed data, it will be possible to provide a close match between simulated and observed voltammograms over the full range of sweep rates. Moreover, this agreement will be possible with only one set of kinetic parameters. Figure 5 shows how Evans's group has used this approach effectively. Often it is easier to rule out a mechanism, because its model will fail to predict responses that resemble the observations for any reasonable set of parameters.

At present, the matching of results with models is usually done by intuitive trial and error, rather than by any algorithm or by any form of artificial intelligence. An important challenge for the new term is to find more systematic means for interpreting behavior, so that expert knowledge is required to a lesser degree.

Perone and his co-workers have shown that pattern recognition, which is discussed in more detail elsewhere in this issue, is capable of addressing this problem. His group has used it to identify overlapping voltammetric peaks,<sup>23-27</sup> to assign mechanisms of electrode processes,<sup>28,29</sup> and to characterize the structures of electroactive compounds.<sup>30,31</sup>





**Figure 5.** Comparison of experimental data (points) to predictions from simulations (curves). The data are for cyclic voltammetry of bianthrone in DMF. Cathodic currents are positive. The simulated model involves two conformers of bianthrone that are reduced at separate potentials. These two conformers can interconvert, and the rate constants for interconversion are obtained from the match between simulated and observed results. Reprinted with permission from Olsen, B. A.; Evans, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 839.

The task of pattern recognition is to classify patterns (i.e., sets) of data into different categories.<sup>32-34</sup> Patterns belonging to known categories are used first to train a computer to correctly identify them. First, the set of data in each pattern has to be defined. Each such set of quantitative features can be regarded as a vector (or a point) in an  $n$ -dimensional space, and the basic assumption of pattern recognition is that vectors for similar patterns will form an isolated cluster in the space. Since the choice of the features (i.e., the elements of data) is empirical, some may have no effect on the classification and some may even cause different clusters to overlap in feature space. Feature selection is necessary to discard useless and confusing features. Once the most effective classification is attained for the training set, the unknown patterns can be classified. The useful features of the unknown pattern are extracted; then, (in work by Perone et al.) the Euclidian distances between the data vector for the unknown and all the vectors in the training set are calculated. The category of the unknown pattern is voted by its  $k$  nearest neighbors, where  $k$  is a small integer.

Perone's group carried out an extended study designed to identify overlapped voltammetric peaks.<sup>23-27</sup> Hundreds of known singlet and doublet voltammograms were used as a training set, with each curve being synthetically generated from the theory of linear sweep voltammetry. Different combinations of reversibility, electron-transfer number, transfer coefficient, peak separation, and peak height ratio were considered, in order to allow broad coverage of possible cases. After considering many features related to peak shape and position, 22 useful features were defined, and weights were assigned for them. The accuracy of classification for synthetic

singlets and doublets was better than 90%. The resolution proved to be 6 mV, a figure that is impossible to duplicate by visual inspection.<sup>23</sup>

Although high accuracy of classification was attained, the needed features of each voltammogram were difficult to define and extract, and some are very sensitive to noise in real data. The procedure used for feature extraction in that study is not general. Instead, it varies with the type of data and the goal of the classification procedure. An alternative approach is to carry out Fourier transformation of the voltammogram.<sup>25</sup> The Fourier coefficients can then be used as features. Since the voltammogram contains mainly low-frequency components, relatively few Fourier components are needed to define the data fully. This procedure of feature definition and extraction is very general, and the discarding of the high-frequency coefficients advantageously reduces the noise level. Perone et al. found that usually fewer features are needed and more accurate classification can be obtained when Fourier coefficients are used as features.<sup>26</sup>

An attractive application of pattern recognition in electrochemistry is the classification of mechanisms. Electrochemical studies are often aimed at characterizing the chemical systems and measuring the kinetic parameters of electrode processes. Kinetic parameters can be extracted from peak potentials and currents in an algorithmic way, but an experienced electrochemist must first look at the shape of voltammograms to gain the subtle information needed for mechanistic assignment. This nonalgorithmic examination of shape forms the basis of pattern recognition in mechanism classification. Complex electrode processes, e.g., those involving adsorption, amalgam formation and coupled reactions, can be classified effectively.<sup>29</sup> The training sets were derived from theoretical cyclic voltammetric data, with eight different kinds of electrode processes being included. The best results were obtained when Fourier coefficients are used as features. The classification accuracy of mechanism for real systems was higher than 90%, if the shape of the cyclic voltammogram was determined by a single mechanism and this mechanism was present in the training set.

In electrochemistry, pattern recognition is fundamentally useful because valuable information exists in the shape of an  $i$ - $E$  curve. The shape is hard to describe mathematically; hence, diagnosis from shape analysis is complicated. Pattern recognition could therefore become a powerful tool in interpretation of electrochemical data. If a computer is well trained, the recognition can be accurate, and artificial errors in data analysis can be avoided, especially when the interested party is not an expert electrochemist.

One drawback of pattern recognition is that it generally does not provide quantitative information. For example, even if a doublet is identified, the peak separation and the height of each individual peak are still unknown. Deconvolution methods can give much more useful results once the doublet has been diagnosed. Another difficulty is that pattern recognition, at least as developed by Perone's group, puts a great demand on the quality of the voltammetric data used in interpretation. Interpretive methods based on results from more than one experiment need to be developed. An effective approach to this problem will probably have to involve an expert system. To date, however, there has been no development of expert systems for the interpretation of static bodies of electrochemical data. There have been some preliminary efforts aimed at creating an expert system that operates dynamically, and that point leads to the next topic.

#### DYNAMIC EXPERT SYSTEMS

Earlier, we held out the fascinating prospect that one might be able to create software capable of strategic and tactical

decision making, such that it could direct an experimental investigation and provide an interpretation of results. This software would operate on a "dynamic" data set, because it would order new experimental results on the basis of prior results and its own working hypothesis. Early versions would certainly have expert character; hence, we term them "dynamic expert systems" in order to distinguish them from expert systems that operate on invariant data that they have no part in gathering.

Eklund has actually developed a dynamic expert system for electrochemistry.<sup>35</sup> He developed his software on a VAX 11/780 to operate a cybernetic potentiostat like the one described earlier in this article, and it used a multitechnique approach to the investigation of three chemical issues: the stability of a product of an electrode reaction, the  $n$  value of an electrode reaction, and diffusion control of the current. The operator would simply define the issue of interest; then, the VAX would direct the cybernetic potentiostat through a series of cyclic voltammetric and chronocoulometric experiments bearing on the issue of interest. The results were compared with ideal responses, and a voting technique was used to provide a conclusion.

The degree of chemical "expertness" embodied in Eklund's system was relatively low. It did not engage in experimental protocols extending beyond a couple of techniques, and it did not formulate hypotheses for testing with further experiments. Nevertheless, his achievement was substantial, because he provided a general solution to the problem of interinstrument communication by text commands and he developed data structures that are particularly well suited to dynamic expert systems. Basically his research has provided a vision of the kinds of things that one might accomplish with an expert system operating with an instrument capable of an extensive experimental repertoire. Impressive developments of this idea are bound to follow.

An important prerequisite is a set of diagnostics by which decisions can be made. Since the decisions are to rest on a machine, then the diagnostics must be numeric. Therdtteppitak and Maloy have begun to address the systematic development of diagnostics, and they have suggested that the exponent on the time variable will be particularly valuable as a means for distinguishing the rate-controlling elements in an electrochemical process.<sup>36</sup> In the end, the utility of any expert system, static or dynamic, will depend on the reliability of its diagnostics. The serious exploration of new diagnostics is critical to any significant application of artificial intelligence in

electrochemistry.

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## REFERENCES AND NOTES

- (1) Anson, F. C. *Anal. Chem.* **1966**, *38*, 54.
- (2) Lauer, G.; Abel, R.; Anson, F. C. *Anal. Chem.* **1967**, *39*, 765.
- (3) Osteryoung, J. *Science (Washington, D.C.)* **1982**, *218*, 261.
- (4) Lauer, G.; Osteryoung, R. A. *Anal. Chem.* **1968**, *40* (10), 30A.
- (5) Turner, J. A.; Christie, J. H.; Vukovic, M.; Osteryoung, R. A. *Anal. Chem.* **1977**, *49*, 1904.
- (6) Osteryoung, J. G.; Osteryoung, R. A. *Anal. Chem.* **1985**, *57*, 101A.
- (7) Schwall, R. J.; Bond, A. M.; Loyd, R. J.; Larsen, J. G.; Smith, D. E. *Anal. Chem.* **1977**, *49*, 1797.
- (8) Anderson, J. E.; Bond, A. M. *Anal. Chem.* **1981**, *53*, 1394.
- (9) He, P.; Avery, J. P.; Faulkner, L. R. *Anal. Chem.* **1982**, *54*, 1313A.
- (10) He, P. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1985.
- (11) Smith, D. E. In "Fourier, Hadamard and Hilbert Transforms in Chemistry"; Marshall, A. G., Ed.; Plenum Press: New York, 1981.
- (12) Creason, S. C.; Smith, D. E. *Anal. Chem.* **1973**, *45*, 2401.
- (13) deLeeuwe, R.; Sluyters-Rehbach, M.; Sluyters, J. H. *Electrochim. Acta* **1969**, *14*, 1183.
- (14) Rohko, T.; Kogoma, M.; Aoyagui, S. J. *Electroanal. Chem.* **1972**, *38*, 45.
- (15) Hayes, J. W.; Glover, D. E.; Smith, D. E.; Overton, M. W. *Anal. Chem.* **1973**, *45*, 277.
- (16) O'Halloran, R. J.; Smith, D. E. *Anal. Chem.* **1978**, *50*, 1391.
- (17) Grabaric, B. S.; O'Halloran, R. J.; Smith, D. E. *Anal. Chim. Acta* **1981**, *133*, 349.
- (18) (a) Oldham, K. B. *Anal. Chem.* **1972**, *44*, 196. (b) Imbeaux, J. C.; Saveant, J.-M. *J. Electroanal. Chem.* **1973**, *44*, 169.
- (19) Soong, F.-C.; Maloy, J. T. *J. Electroanal. Chem.* **1983**, *153*, 29.
- (20) Feldberg, S. W. *Electroanal. Chem.* **1969**, *3*, 199.
- (21) Maloy, J. T. In "Laboratory Techniques in Electroanalytical Chemistry"; Kissinger, P. T.; Heineman, W. R., Eds.; Marcel Dekker: New York, 1984; pp 417-462.
- (22) Pons, S. *Electroanal. Chem.* **1984**, *13*, 115.
- (23) Sybrandt, L. B.; Perone, S. P. *Anal. Chem.* **1972**, *44*, 2331.
- (24) Pichler, M. A.; Perone, S. P. *Anal. Chem.* **1974**, *46*, 1790.
- (25) Thomas, Q. V.; Perone, S. P. *Anal. Chem.* **1977**, *49*, 1369.
- (26) Thomas, Q. V.; DePalma, R. A.; Perone, S. P. *Anal. Chem.* **1977**, *49*, 1376.
- (27) DePalma, R. A.; Perone, S. P. *Anal. Chem.* **1979**, *51*, 825.
- (28) DePalma, R. A.; Perone, S. P. *Anal. Chem.* **1979**, *51*, 839.
- (29) Schachterle, S. D.; Perone, S. P. *Anal. Chem.* **1981**, *53*, 1672.
- (30) Burgard, D. R.; Perone, S. P. *Anal. Chem.* **1978**, *50*, 1366.
- (31) Byers, W. A.; Freiser, B. S.; Perone, S. P. *Anal. Chem.* **1983**, *55*, 620.
- (32) Jurs, P.; Isenhour, T. "Chemical Application of Pattern Recognition"; Wiley: New York, 1975.
- (33) Wilkins, C. L.; Jurs, P. C. In "Transform Techniques in Chemistry"; Griffiths, P. R., Ed.; Plenum Press: New York, 1978.
- (34) Kowalski, B. R.; Bender, C. F. *J. Am. Chem. Soc.* **1972**, *94*, 5632.
- (35) Eklund, J. A., Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1984.
- (36) Therdtteppitak, A.; Maloy, J. T. *Anal. Chem.* **1984**, *56*, 2594.

## Microelectronics in Analytical Chemistry

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Although small computer systems have impacted the practice of analytical chemistry by their ability to help capture and electronically manipulate data in traditional ways, even greater effects of this microelectronic revolution are becoming apparent. First, microelectronic fabrication techniques are being used to make new classes of transducers. Second, new integrated circuits are being developed that allow the chemist to correlate, convolve, and domain convert data both before and after capture by the computer. These front-end and back-end processing elements open up the world of small computers to techniques usually requiring large mainframe processors. Third, arrays of nonspecific sensors are being used that are based on solid-state detectors and chemimetric techniques. Finally, new classes of self-optimizing instruments are being created. Typical examples from each of these areas are presented.

Small computer systems and microelectronic components give the scientist a new set of tools for the laboratory. In-

creasing evidence shows many laboratories are beginning to use these tools to perform experiments in novel ways, often