DEVELOPMENTS, TRENDS AND COMMERCIAL AVAILABILITY OF INSTRUMENTATION (HARDWARE AND SOFTWARE) IN MICROCOMPUTER BASED VOLTAMMETRY

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Voltammetry is an important electrochemical technique which is used extensively to solve problems in many areas of chemistry. Since the method is based on the use of current–potential–time curves, voltammetric instrumentation is highly suited to computer based forms of technology. In this article, an overview of existing hardware and software that have been used to facilitate improvements in computer based voltammetric instrumentation is provided. It is concluded on the basis of this survey that developments to date in the use of computer based technology have been conservative relative to those in spectroscopic forms of instrumentation. Consequently, it is postulated that a new generation of more "intelligent" voltammetric instruments would become available immediately if the full power of presently available digital hardware and software were to be implemented as has been the case with some other forms of instrumentation.

1. INTRODUCTION

In many scientific disciplines, the instrumentation has evolved through several generations of design from manually operated to fully automated systems. In the field of voltammetry (polarography*) the early instrumentation designed in the 1920s was inherently simple by today's standards, although relatively advanced compared to many other forms of chemical instrumentation. Typically, the two electrodes used were a dropping mercury working electrode with either a mercury pool quasi reference electrode in a one compartment cell or a calomel reference electrode in a two compartment cell electrically connected by a salt bridge. Commonly, a voltage (constant DC potential) was applied across the working and reference electrodes with the aid of a potentiometer type circuit and the direct current flowing through the cell as a result of the applied voltage was measured with a galvanometer. The individual sets of current–voltage data points were recorded in a note book by the scientist using the instrument and subsequently a DC polarogram (voltammogram) was constructed manually from these data points. From this graphical representation of a polarogram, the half-wave potential, $E_{1/2}$, and the limiting current i_l were calculated. $E_{1/2}$ was related to the species undergoing reduction or oxidation and i_l was proportional to the concentration. Figures 1 to 3 provide examples of early circuit diagrams, polarograms and related details of the instrumentation and experimental arrangements. The polarograms shown in these figures were recorded by photographic techniques.

The evolutionary process over the first 50 years of the history of voltammetry saw the advent of numerous alterations to the instrumentation introduced as advances in electronic circuitry occurred. Examples relevant to DC voltammetric methods included: (i) the introduction of a Wheatstone bridge circuit to measure the cell resistance and then correct for ohmic *IR* drop, (ii) automated application of the voltage using a slowly changing DC potential, (iii) automated recording of the DC current, (iv) automated recording of the current–voltage curve on X–t and then X–Y recorders, (v) introduction of the three electrode potentiostat to minimize uncompensated resistance, (vi) use of positive feedback circuitry to minimize uncompensated resistance still present when a

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* Polarography is a special name given to the technique of voltammetry when a dropping mercury working electrode is used.

potentiostat is used, (vii) automatic compensation for charging current and other background currents, (viii) automatic recording of the derivative of the current–voltage curve.

Developments in electronics during the 1940 – 1970 period also enabled transient techniques to be added to the voltammetric methodology, e.g. alternating current, square wave, pulse, linear sweep voltammetry, etc. Many of these techniques could not have commenced with a manual stage equivalent to that described above for DC polarography, as the time scale required for measurement is too short to be monitored by the human eye, which, in a sense, was the original voltammetric recording device. That is, advances in instrumentation usually enabled both existing methods established with older forms of technology to be improved (e.g. development of derivative DC voltammetry) and new techniques to be introduced (e.g. transient voltammetric methods). Importantly, the advent of operational amplifiers[1] and integrated circuits and transfer of this technology into commercially available voltammetric instrumentation contributed greatly to the in reviving interest in applications of voltammetry in the period 1950 – 1970.

In the last two decades, digital electronics and computers have made a substantial contribution to advances in voltammetric instrumentation. In the early stages of commercial development of digital voltammetric instrumentation, the existing analogue approaches were simply mimicked, unlike the situation in spectroscopy where the new powers of the digital era was more fully exploited at an early stage of digital electronics. The evolutionary process with digital instrumentation has now continued to the point where artificial intelligence or decision making capability can be included in the instrumental design. Expert systems and use of chemometric methods in on-line modes are now forthcoming and much hardware could now be rendered obsolete by substitu-

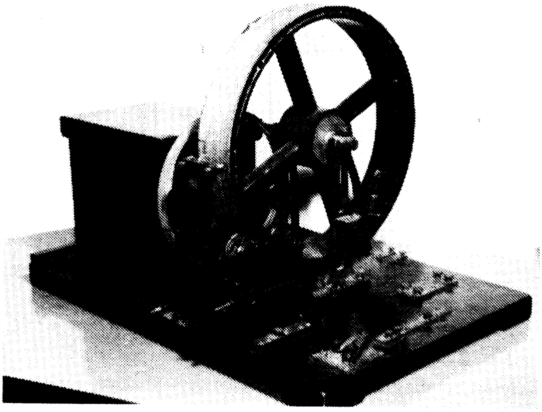


FIG. 1
Photograph of the original polarographic instrument built by J. Heyrovský in 1924. Reproduced by courtesy: The Archives of the Academy of Sciences of the Czech Republic

tion with software or mathematical functions or equivalent digital logic circuit descriptions. Unfortunately, this latest revolution has not yet appeared to any significant extent in commercially available voltammetric instrumentation and many of the most recent concepts still need to be translated from research laboratories where significant advances along these lines have occurred.

The theory of most of the hardware required for voltammetric experiments and many electrochemical processes occurring at the electrodes can now be simulated to a high degree of precision. Thus, it can be postulated that if the full power of digital electronics and digital simulation were to be coupled with the concepts of robotics, artificial intelligence, pattern recognition, expert systems and chemometrics, then a completely stand alone voltammetric system could undertake in a completely automated fashion tasks such as (i) identity and remedy faults in electrodes and electronic circuitry, and (ii) determine the optimal waveform and method of data analysis for a particular problem. With introduction of the latter concept, there would be no need to sequentially undertake pulse, square wave and alternating current experiments as part of the analytical methodology used to decide what voltammetric technique is the most sensitive or provides the required resolution for a particular problem. A new generation of smart instruments might apply a multi-time domain (or frequency domain) test waveform and from this experiment optimize the experiment with respect to back-

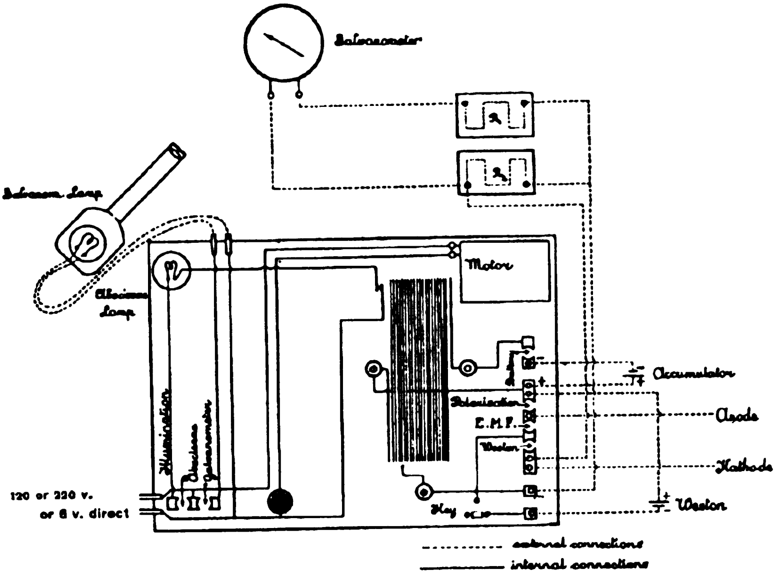


FIG. 2
Schematic diagram of the Heyrovský–Shikata type polarographic instrument manufactured in 1929. Reproduced by courtesy: The Archives of the Academy of Sciences of the Czech Republic

ground current correction, *IR* drop correction, establish the mechanism, deconvolute overlapping peaks and other forms of interference, etc., and if necessary, design and perform the next experiment if this is required to achieve a preset goal, with a full statistical analysis of the result being part of the final data report to confirm or otherwise that the goal has been achieved. With this approach, no longer would the electrochemist need to be concerned with the distinctions between the plethora of methods now on the menu list of most commercially available digital voltammetric instruments: e.g. square wave voltammetry, alternating current voltammetry, double potential step chronocoulometry, chronoamperometry, differential pulse voltammetry, normal pulse voltammetry, etc. The smart instrument, which hopefully will be available in commercial form by the end of this century should revolutionize our thinking about voltammetry and be able to utilize in close to real time the well established mathematical foundation already established for voltammetric instrumentation and experiments. At present, implementation of voltammetric experimental procedures are generally very inefficient and require inordinately long periods to produce even close to optimal results.

In the belief that concepts related to voltammetry will undergo revolutionary changes during this decade if the power available via the use of digital methods are introduced into commercially available instruments, the authors have tried to present an overview of the present foundation available on which future generation voltammetric information might rely, and then to reflect on what form the smart voltammetric instrumentation of the future might take. The article, of course, actually reflects only the authors incomplete awareness of what might happen if the convergence of several expanding areas of knowledge in the disciplines of mathematics, electronics, computing, statistics

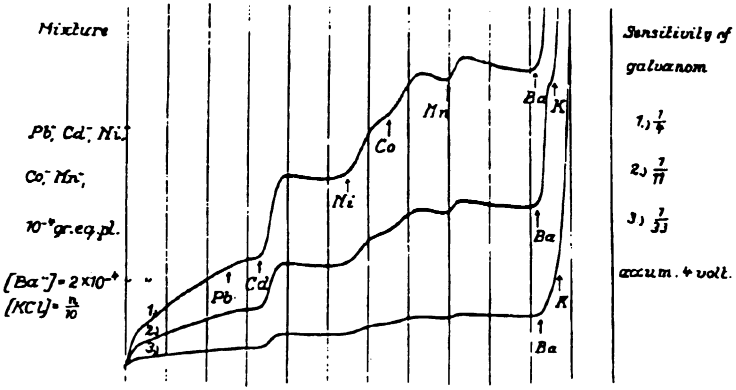


FIG. 3

A polarogram recorded on the instrument described in Fig. 2. Reproduced by courtesy: The Archives of the Academy of Sciences of the Czech Republic and physics in addition to the authors' home base of chemistry are all focussed on voltammetric instrumentation. In this sense, the article contains considerable speculation and in a statistical sense is very unlikely to be accurate in predicting the future. However, the authors do believe that it is time that voltammetric instrumentation shed its presently conservative armour and we hope that this article may at least encourage a more radical approach to commercial development so that by the end of the decade the instrumentation will be of a standard appropriate for the start of the 21st century.

The subject of "Computerized Scientific Instrumentation" has developed a language of its own. As an aid to understanding the language, a few commonly used terms need to be understood and are therefore defined in the introduction. For example, *Computer Based Instrumentation*, is a general term, used to describe a group of measuring and control instruments managed by any kind of computer, e.g. the term computer based voltammetric instrumentation is frequently used to describe a group of voltammetric experiments managed by a laboratory computer or a microcomputer. *Personal Instrument (PI)* or *PC-Based Instrument (PCBI)* are terms used where a personal computer (PC), with its operator control and display function, is an integral part of the instrumentation. This is the most common form of present day commercially available computer based voltammetric instrumentation. PC-based instruments are available in formats such as (i) stand-alone modules, each having their own housing and power supply, and (ii) plug-in cards, which can be inserted directly into a free expansion slot of a microcomputer.

2. COMPUTERIZED VOLTAMMETRIC INSTRUMENTATION

2.1. *The Role of the Microcomputer*

It is likely that almost any smart of intelligent voltammetric system built for use in the 1990s will contain a range of analogue and digital electronic components coupled to a microcomputer. The incorporation of a microcomputer or multiple sets of microcomputers into scientific instrumentation enables the development of program-controlled systems whose function and performance then depends to a large extent on the quality of the software. While there is no doubt that the pheripheral hardware will continue to become faster during the present decade and parallel processing systems should become widely available which will also speed up many features of the computing, it is the advent of new software that should provide the most obvious changes to commercially available forms of voltammetry in the 1990s.

Typically, the introduction of more powerful software into commercially available microcomputer based instruments in the 1990s should mean: (i) an improvement in the accuracy and speed of measurements, (ii) an increase in data throughput, (iii) automated preparation of the samples (e.g. by robotics), (iv) improved planning and control of experiment data acquisition and data handling, (v) the introduction of new forms of calculations involving for example, application of statistical methods, digital smoothing and transformation of data, (vi) the saving and printing of results in more efficient formats, (vii) taking advantage of powerful graphics packages, exploiting data bases and employment of methods of artificial intelligence and chemometrics.

Different approaches to the design of microcomputerized electrochemical devices or workstations have been employed in the last 20 years. At the beginning of the microprocessor era, many laboratory designed electrochemical systems were "home made" measuring systems. Typically, such systems contained built-in microprocessors or microcomputers placed into separated boxes and interfaced to the analogue components of the instrumentation. This is the "modular" format. More recently, dedicated computerized "Electrochemical Systems" have been made available commercially for frequently used electrochemical methods. With these systems, designers have had the resources to combine products from a range of manufacturers to produce stand-alone subsystems or even complete stand-alone turnkey systems with supporting software. These are the so called "user friendly" systems.

It is not surprising that since inexpensive, reliable and powerful personal microcomputers are readily available that they are widely used in electrochemical instrumentation. The modern computerized electrochemical experimental workstations is, in fact, a combination of many different devices controlled from a personal computer via an IEEE-488 or other standard input/output device. In the case of simple experimental workstations, multifunction programmable expansion boards are used to build up the workstation. The expansion boards are installed internally in an expansion slot of the Personal Computer and convert the computer effectively into system control, data acquisition, and signal analysis instrument.

2.2. *Computerized Voltammetric Instruments Using Subsystems Separated from the Microcomputer*

Many computerized electrochemical systems use subsystems individually linked to the microcomputer. These external subsystems mainly expand the input/output (I/O) capability of the whole system and are used for control of the electrochemical workstation and experimental data acquisition. If an internal bus of a microcomputer is used to communicate to the external subsystem, then the subsystem must be located very near to the computer bus to avoid undue disturbance (noise) in the system. The necessary collaboration of the operations of the external subsystems and the microcomputer may be achieved, for example, by utilization of an interrupt system, direct memory access (DMA) or addressing of subsystem circuits at a microcomputer memory place.

Larger external subsystems are obviously likely to have their own "intelligence" achieved with a microcomputer which contains memory for temporary saving of data, etc. Communication of these computerized external devices with a host microcomputer usually are carried out via either a serial port (e.g. RS-232, RS-423, RS-485) or an

IEEE-488 bus (a GPIB – General Purpose Interface Bus) or an HP-IB bus (Hewlett–Packard Interface Bus) or ANSI MC 1.1 and IEC 625-1 standards, or IMS2, etc.). With this form of communication, the distance between the subsystem and the host microcomputer can be much longer than is the case for a link over the internal bus, but the data transfer rate is lower. Sometimes this means that a "bottleneck" problem has to be solved when real time transfer of the experimental data is needed without data concentration or data saving in the memory of the subsystem (e.g. with fast scan rate cyclic voltammetry). Some GPIB controllers (e.g. AT-GPIB, GPIB-PCIII, and MC-GPIB from National Instruments) allow the data transfer to occur at speeds up to 1 MB per second GPIB reads and writes[2]. This speed is achieved with a custom high-speed CMOS Turbo488 ASIC (Application – Specific Integrated Circuit) device which employs bidirectional FIFO (First-In-First-Out) memory under DMA control and an IEEE488.2 controller chip (NAT4882). If the whole system is dedicated to automated electrochemical measurements, then the term "Electrochemical Interface" may be used to describe the external subsystem.

Typical examples of the external data acquisition and control interfaces that could be used in an electrochemical instrument are: the ACRO-900 from Acrosystems[3], the 7000 MDAS from Trans Era[4], the Isaac 41-I, 91-I, 2000, and 5000-MP from Cyborg[5], the DASA 9000 from Gould[6], the PCI-3000 and others from Burr–Brown[7], several μMACs and the MACSYM from Analog Devices[8], the ACU from Mowlem Microsystems[9], the DAS Series 500 (e.g. Models 500A, 500P, 556 and 570) from Keithley[10], the L8200 from Linseis[11], the MPC Systems from Preston Scientific[12].

Serial communication with the host microcomputer is used mainly for remote data acquisition devices and for laboratory and industrial data loggers/process controllers. For such complex tasks, the following devices may be used: the ORION delta 3530 and IMPs 3595 series from Solartron Instruments[13], the Datalogger 3000 from Digitec[14], the Compu DAS from Signal Laboratories[15], the SC581 from ERO Electronic S.p.A.[16], the AD 5311, 5312, 2200, 2240, and 2280 Series from Fluke[17], the 230A from Doric Scientific[18], the System 10 Data PAC from Daytronic[19], the RIM-1000 from Novatech[20], and the MIT 350 from Metra Blansko[21].

Several devices have the input circuits for low level signals and A/D conversion in a separate enclosure with the part containing the digital circuitry being installed internally into an expansion slot of an IBM PC/XT/AT or compatible PC. Typical examples are LAB MASTER DMA from Scientific Solutions[22] or the Model 553 Potentiostat from AMEL[23]. With this approach, the sensitive parts of the circuitry are isolated from electrical noise within the computer.

General workstations, based on a "Personal Instrument" (PI) or "PC-Based Instrument" (PCBI) approach, may be used for computerized data acquisition, control and test applications. In the case where separately housed stand-alone devices are controlled from a microcomputer, the whole system may be linked together by an IEEE-488 bus or equivalent. These readily rearranged systems are very flexible and therefore used in many laboratories. Typical examples of such devices are: the HP 3421A, 3497A, 3852A, 6940B, 6942A, 6944A and HP 61010AA – HP 61017AA from Hewlett–Packard[24] and several B3000 PC-Based Instruments from Siemens[25].

2.3. *Examples of Commercially Available Computerized Voltammetric Instrumentation Based on Subsystems*

Commercially available systems for "Computer-Assisted" or "Computer-Aided Electrochemistry" belonging to the class of PI or PCBI devices include:

Tacussel: The Polaro-computer systems TAC 78, TAC 2000 and the Z-Computer/UC system for impedance measurements or the Programmable Interface Unit IMT 1 collaborate directly with Hewlett–Packard desk top computers (e.g. HP 98580B) together with a Potentiostat–Galvanostat device from the PJT family from Tacussel[26]. The Tacussel company supports the electrochemical measurements by software such as LOGICIEL-A, IFV/IMT/IBM and IFC/IMT/IBM.

EG & G – Princeton Applied Research Corporation: The EG & G PAR Model 173 Potentiostat–Galvanostat (with the Plug-in Interface Model 276) or the Models VersaStat, 263, and 273A Potentiostat–Galvanostat may be used to perform many electrochemical methods provided suitable software is purchased from the manufacturer[27]. For example, Corrosion measurements may be supported by the Model 332 SoftCorr Corrosion Software package. The Model 270-1 Electrochemical Analysis System has been designed to enable users of varying electrochemical expertise to perform measurement rapidly and accurately. The system is flexible enough to provide a high degree of user fine tuning and provides access to over 20 electrochemical techniques.

Solartron: The Solartron 1286 Electrochemical Interface[13] and a controlling microcomputer are coupled with a software package for electrochemical measurements. The 1090 Data Management System, used in conjunction with the 109001 Electrochemical Analysis Application Module, provides a complete package for the control of the 1250 Frequency Response Analyzer and as well the 1286 Electrochemical Interface for AC impedance measurements. The potentiostat drives two, three or four electrode electrochemical cells. Experimental data are measured with two DVM subsystems (from $3^1/_2$ to $5^1/_2$ digit precision) and the automatic IR compensation has two modes.

AMEL: The Potentiostat Model 553, extended with an I/O Apple II interface is produced by AMEL[23]. The Potentiostat is controlled from an Apple II 8-bit microcomputer by calling the subroutines from the firmware (two 2716 EPROMs) provided with the Model 553 instrument. AMEL also manufacture the completely computerized Model 433 Polarographic Analyzer which includes a built-in microcomputer based on the Z80-A CPU. This analyzer is linked by the serial interface to an external host personal computer which controls all functions of the analyzer. A static mercury drop electrode and the analyzer have been integrated into a single, compact package. The System 5000, also supplied by AMEL, utilises an interface based on a 68070 microprocessor and 128 KB of program ROM Firmware and 128 KB of CMOS RAM with battery backup. The software packages EASY SCAN (voltammetry) and EASY CORR (Corrosion) software are available for use with the system 5000. This system is similar to the EG & G PAR Model 273, but offers additional flexibility and therefore access to an even wider range of electrochemical techniques.

Czechoslovak Institute of Metrology: The computerized Electrochemical Analyzer PEA-12 was a system developed by the Czechoslovak Institute of Metrology[28] in which the electrochemical interface was controlled by the 8-bit microcomputer PMD-85 which was based on a 8080 microprocessor. The EP10 system produced by HSC Servis[29] is a recently modified version of this sytem.

Cypress Systems: The Model CYSY-1 Electroanalytical System from Cypress Systems[30] contains an electrochemical interface which is linked to a PC of the IBM AT type. The software is installed on the computer hard disk. The Model CYSY-1B is the basic system with current-measuring full scale ranges from 5 mA to 78 nA and the Model CYSY-1H is the high-sensitivity system with ranges from 5mA to 2 nA. The Model CYSY-4 computer-controlled in vivo electroanalytical system is specially designed for simultaneous measurement of neurotransmitter concentration levels with microelectrodes.

Eco Chemie: The AUTOLAB System from Eco Chemie[31] is the generic name of a range of electrochemical instruments controlled by a Personal computer. The Electro Analytical System AUTOLAB/EAS is designed for voltammetry and polarography. The EAS software can be used for several electrochemical techniques. The AUTOLAB/GPES is General Purpose Electrochemical System controlled by the GPES software package. The AUTOLAB System also provides access to impedance spectroscopy (using the Fast Fourier Transform method) and automatic titrations.

Polaro-Sensors: The Eco-Tribo Polarograf is the electrochemical device for polarography and voltammetry controlled by personal computer with plug-in A/D and D/A card provided by Polaro-Sensors[32]. The analog part of the instrument (potentiostat, current–voltage converter, etc.) is located within the electrode stand. A novel pen-shaped mercury capillary (mini- and micro-drop) electrode is used with this instrument.

2.4. *Examples of Commercially Available All-In-One-Box Computerized Voltammetric Systems*

Compact and dedicated electrochemical devices with built-in microcomputer constitute another group of voltammetric instrumentation. These systems represent stand-alone computerized devices with their software being in the firmware or on a diskette. They can usually be interfaced to a host computer for tasks requiring extensive data handling and storage.

Some of the companies which produce or have produced devices based on the all-in-one-box systems and their products are listed below.

EG & G Princeton Applied Research Corporation[27]: Models 350, 374, 384A and 384B which can be used with the Model 303 and 303A static mercury drop electrode.

Sargent–Welch[33]: The Model 7000 instrument.

Metrohm[34]: The model 646 VA-Processor combined with the Model 647 VA-Stand.

ZWG[35]: The ECM 700 system.

Spectroscania[36]: The VOLTAMAT system.

Bioanalytical Systems[37]: The BAS-100 and BAS-100A Electrochemical Analyzers. These instruments may be combined with a very sensitive I/E converter when small currents need to be measured as is the case with voltammetry at microelectrodes.

Tacussel[26]: The digital polarographic analyzer POL220T.

2.5. *General Purpose Systems that can be Readily Adapted for Computerized Voltammetric Measurements*

The PCI-501H Series PCI Work Station for data acquisition, test, measurement and control from Burr–Brown[7] belongs to this category devices as did the Iskra-226 Work Station from the U.S.S.R. (ref.[38]). The Iskra-226 had a 16-bit main processor and 8-bit 8080-type processor for communication and contained a data acquisition and control interface but did not include a potentiostat or a galvanostat or a current/voltage converter and did not have any electrochemical software. However, the Iskra-226 was often used to develop electrochemical instrumentation in the U.S.S.R. because the computer has been designed to be a general data acquisition and control system and was provided with a powerful graphic version of a BASIC interpreter.

Obviously, general purpose data acquisition systems of the above kind must be converted into an Electrochemical Interface by addition of the following:

a) a potentiostat or a galvanostat or both;

b) a circuit for a measurement of a current of both polarities (e.g. a current/voltage converter) over a very broad range (at least from 10^{-3} to 10^{-8} A FS–Full Scale). The Iskra-1081 system has been planned to be like an Iskra-226 system with these add-on devices built-in into a single box together with a microcomputer of the IBM XT type.

Circuits for driving electrochemical cells with potentiostats or galvanostats (D/A converters) and for data acquisition (e.g. multiplexers with filters, sample and hold circuits and A/D converters) easily can be designed to provide the necessary accuracy and speed required for electrochemical measurements. However, improvement in these circuits via exploration of the use of faster D/A and Flash A/D converters will continue to improve the speed of the computer based software of the electrochemical instrumentation. Ultimately, the rise time of the potentiostat or galvanostat/electrochemical cell systems as well as the speed of current/voltage converters may become more and more important in determining the overall quality of the resulting electrochemical measurement, although it is probable that software approaches to correct for imperfections introduced by hardware will be introduced more widely, e.g. the electrochemical cell transfer function will be determined and the response deconvoluted from instrumented artifacts.

2.6. *Board Level Interface Cards*

A board level product is a single printed circuit card that fits into one of the expansion slots of the personal computer (also Plug-In or Add-On-Cards). The card provides a rear connector for attaching input and output signals. These cards, available from a number of manufacturers, to specifically communicate, for example, with the IBM inner XT, AT or microchannel bus, contain all the circuitry necessary to perform the supporting tasks in electrochemical instrumentation. Commonly available interface cards used for laboratory instrumentation based on the use of IBM XT or AT microcomputer systems (mainly for data acquisition and control systems, digital signal processing) include the precision analog interface board DM-100 and AT/MCA CODAS System (hardware and software) from Dataq Instruments[39], the boards of the RTI-200 and RTI-800 series from Analog Devices[8], the PCI-20000 System from Burr–Brown[7], the PC-series from Boston Technology[40], the DACS card from IBM[41], and the DT2800 and DT2900 series from Data Translation[42]. The DT2841 group boards are a set of high speed analog and digital I/O boards for the IBM AT systems. These boards provides 12- or 16-bit A/D input, two 12-bit D/A outputs and 16 lines of digital I/O. The DT 2841-L board which is a member of the "DT-Connect" interface specification family can be plugged into the DT7020 Floating-Point Array Processor board and so achieves 12-bit A/D throughput to 750 kHz. Other board level products are: the DAS, DAC, PIO, PDMA, PDISO, COM, MBC-488, IE-488, etc., and PCIP Personal Computer based Instrumentation Product cards from MetraByte[43], the PC-LabCard series from Advantech[44], the ACJR, ACPC, ACAO, PERSONAL488, etc. cards from Strawberry Tree[45], AT- or MC-cards (e.g., AT-MIO, AT-DIO, AT-GPIB, etc.) from National Instruments[2], the DAC-12 from SONFAT[46], COMET- and FLASH-systems with ACPC and ACAC cards from Ziegler[47], the MARVIN card from HEC[48], the Model 25 (with DSP) from Dalanco Spry.[49], the KXB-20115 from Kenda Electronic Systems[50], the RW series of interface boards from Laboratory Software Associates[51], the ADC-10 and mADC030 boards from Contec Microelectronics[52], the CIO-AD16 (compatible with MetraByte DAS-16 and PIO-12) from Computer Boards[53], the Data Acquisition Processor DAP from Microstar Laboratories[54], the Multi-LAB and MODULAR-4 boards from SORCUS Computer[55], the R6100 board from Rapid Systems[56] for a 25 MHz 8-bit data acquisition, the PC-TEST series product line from Soltec Corp.[57], the 5508HR card from the Direct Connect Series of the ADAC Corp.[58], DAC, DAS, LSDAS, MSDAS, HSDAS, and FAST data acquisition boards from Analogic[59], the CompuScope 220, 250, and LITE from GaGe[60], AD and ADA series of boards supported with RTD Linx, RTD LabLinx, and Atlantis software drivers and tools as well as Signal*Math and Pegasus programs for data acquisition and digital signal processing from RTD[61], ADDIALOG and ADDIMULTI PA boards with Signal-tools and Rubens data acquisition and processing software from ADDI-DATA[62], AIP, ADC and AOP cards from Blue Chip[63], AD and DA cards from Kolter Electronic[64], the 8- and 14-bit ADX cards from Wilke Technology[65]. PC-AN cards from Daytronic[19], PC-ADC, PC-DAC, and PC-LAB analog boards (supported by DigiTools routines) from Digimetric[66], the high speed data acquisition board Model CS250 (for 100 MHz sample frequency) from Industrial Computer Source[67], PC-family of analog cards from Datel[68], the Model 410 board from TransEra Corp.[69], the ACP1 board (data coprocessing provided by an Inmos T800 Transputer) from Signalysys Ltd.[70], the data acquisition boards AX54 and AX56 from AXIOM[71], the LAB TENDER, DADIO, MC-DAS 1612 and MC-DAS 1616 from

Scientific Solutions[22], the AIO, STR, AOB, ML and PC card families from Industrial Computer Source[72], the IFAD12 and IFADD12 from Electronic Solutions[73], the MC-, ME- and MIO-card families from Meilhaus Electronic[74], the ADC-01 and ADC-02 from Tesla Strašnice[75], the MCI- and PCI-card families with MCID- and PCID-software drivers and disyLog and disyLab data acquisition, control and data-signal processing packages from disys[76], and PCS/96002 System Board (with Motorola DSP 96002 processor) and as well TMS320C30 Processor Board (with Texas Instrument's DSP) from LSI[77] have two channels of 16-bit A/D and D/A conversion. Many other cards with the digital signal processor (DSP) together with their signal-analysis software also can be used for data acquisition and data handling in electrochemistry. Several examples of these DSP hardware and software combination are reviewed in refs[78,79].

Cards for communication and control containing serial, parallel, IEEE-488 and other interfaces also are produced by several manufacturers. These interface cards as well as special cards for support of calculation, digital signal processing, frame grabbing and frame processing, image processing, etc. are not specifically listed here, but of course are used in the electrochemical instrumentation field.

3. WORKSTATION CONTROL AND DATA ACQUISITION

Activities undertaken with many electrochemical workstations e.g., purging oxygen from solution with nitrogen and dislodge and dispensing of mercury drops in polarographic instrumentation can be simply controlled from the computer by on-off signals, e.g. with TTL levels. The necessary quality of a potentiostat (galvanostat) is usually readily available when a throughput of less than about 30,000 12-bit measurements per second is employed. The potentiostat, together with several additional circuits for timing, synchronization of measurements and interruption and the digital electrochemical interface provide the basis of a powerful tool for computerized electrochemical instrumentation. The majority of common electrochemical methods are then achieved only by selection of appropriate software. A control program prepared in assembly language or even the high level C language can be used to reach the 30,000 12-bit data acquisition rate mentioned above. Control programs prepared in most other higher languages are much slower and their maximal data acquisition rate is in the range of hundreds to thousands of measurements per second, which is inadequate for some areas of electrochemistry.

When electrochemical parameters need to be measured at high speed and accuracy, improvements in both the software and hardware are required and an appropriate electrochemical interface has to be designed. Very fast D/A and A/D (mainly flash) converters are available (higher cost) but it is a more difficult task to speed up the overall function of the whole system: e.g. the electrochemical cell with a galvanostat or potentiostat and a current/voltage converter. Many problems have to be solved at short electrochemical time domains e.g., the whole system stability needs to be improved, the potentiostat slew rate may be inadequate, output voltage and current range may need to be changed and charge injection, solution resistance, the inductance of leads etc. may all need to be seriously considered. It also needs to be remembered that fast data transfer from the A/D converter into memory must be used. When, DMA transfer is used, the possibility exists of acquiring the data by a background program and using a foreground program to present real time graphical display of the experimental data. With very rapid experiments, it may also be sensible to introduce discrete digital circuitry to control the initial switching and final potentials of say a fast scan cyclic voltammogram and the voltage step polarity, etc. instead of relying on program control[80]. When extremely high data acquisition rate of analog input signals are required only signals from one channel can be used. Measurement of multiplexed analog signals as often employed with slow time domain electrochemical measurements, slows the signal throughput as the settling time for each channel measured must be allowed for.

Further improvements in data acquisition speed, real time data handling and other functions are supported by new 32-bit microprocessor systems, some of which have the RISC (Reduced Instruction Set Computer) architecture. Additionally, implementation of high speed digital signal processing (DSP) chips (e.g. Analog Devices' ADSP-21020 IEEE Floating-Point microprocessor[8]) for application of real-time filtering, FFT and other transformations will contribute greatly to many aspects of pulse, AC and convolution voltammetry.

Data acquisition circuits must accept input data (e.g. voltage or current) over many orders of magnitude. Therefore, the gain of the input signals needs to be properly set. This can be set manually, from the computer program or automatically by autoranging. Autoranging circuitry sets the gain of the system sequentially[81,82] until the system reaches the maximal output data value (still within the full scale range) to achieve the highest accuracy of the overall measurement.

There is obviously no difficulty with autoranging when the measuring method can be allowed to wait until the right range is selected. This is the case in polarography. However, if a system is being studied where measured data are dependent on the previous "history" of the experiment and that measurement cannot be interrupted to wait until the new right range is set without modifying the experiment (e.g. cyclic voltammetry), the computer controlled sequential autoranging cannot to be used. In this case, the proper range must be selected before the experiment is commenced. Difficulties during measurement of a noisy signal can also arise with autoranging because the system could switch the gain forward and backwards repeatedly. To solve this problem, higher resolution A/D conversion (e.g. 16-bit) and use of a lower gain range for whole experiments can be employed. However, a better way to remove this problem is to use a floating-point converter, e.g., the MN 5420[83]. With this approach an effective 20-bit dynamic range is achieved with 12-bit accuracy. The 22-bit Floating-Point ADC Module ADC750 (116 dB dynamic range, 400 kHz sampling frequency) from Burr–Brown[7] is the first commercially available product of this type.

Considerable advantage is realised in the field of chemical microinstrumentation[84,85] when new monolithic or hybrid technologies are applied to the miniaturization of sensors and their support circuits to improve the output signal acquisition and processing. This approach could be more widely achieved with electrochemical computerized instrumentation.

4. NOISE

If 10-bit, 12-bit or even higher accuracy need to be obtained with the computerized electrochemical instrument then the noise level in the whole system (e.g. the D/A converter, the potentiostat, the electrochemical cell, the I/E converter, the multiplexer, the sample and hold, A/D converter etc.) must be kept at a suitably low level to achieve the signal-to-noise ratio required to achieve the specified accuracy.

Within and external to the whole system, there are different sources of a noise. Three basic forms are:

a) transmitted noise which is received together with the normally expected signal (e.g. noise generated by an electrochemical process);

b) intrinsic noise (e.g. popcorn and shot noise, glitches from D/A converters);

c) interference noise picked up externally to the circuits which may be due to natural disturbances (e.g., lightening) or from coupling effects with different parts of the system or the environment (e.g. pickup from the mains power supply or the close proximity of transformer powered devices controlled with SCRs or triacs, switching power supplies, radio and TV transmitters), or from the so-call "Digital Noise" associated with the present of multiple digital circuits in the interface, computer and its monitor, etc.

With large amplitude pulse methods (pulse voltammetry, etc.), the measurements are usually broad band ones and the task of suppressing noise is relatively difficult. Despite the fact that many endeavours to achieve a suitable low level of a noise could be based on theory, noise minimization methods are usually based mainly on the experience of the designers. The noise can be catalogued under the following headings[86]: common-impedance noise, capacitively coupled noise, magnetically coupled noise, power-line transients and miscellaneous sources of noise.

The design strategy to minimize noise starts with the selection of the electronic elements (e.g. standard TTL circuits are noisier than CMOS circuits) and their layout on a printed circuit board, separation of "grounds" (e.g. digital ground, analog ground, the ground for control and power elements, actuators, grounding of metal parts and boxes, etc.), shielding and guarding[86 - 89].

For additional improvements in the signal-to-noise ratio, several other possibilities also are available[90 - 92]:

a) To repeat the measurement several times in order to suppress random noise (e.g. measuring and averaging results from several pulses, or from a number of perturbations applied to the same mercury drop or repeating and averaging the same measurement on several new mercury drops). This method is often called ensemble averaging.

b) Measuring by an integrating method synchronized exactly to the time interval of a single or multiple line period of the mains frequency to depress mains power influence upon our measurements, e.g. integrate over 20, 40, 60, 80 or 100 ms periods if the mains frequency is 50 Hz.

c) To suppress unwanted factors (e.g. the charging current) the measuring method must be applied in a suitable fashion. The techniques of square wave polarography[93], pulse polarography[94], differential pulse polarography[95,96] and the differential integrated multiple pulse polarography[97,98] are excellent examples of this approach.

Our practical experiences with several data acquisition cards located in the expansion slot of a PC shows that errors of repeated single measurements are about 1 LSB for 12-bit conversion when an input signal is in the ±10 V FS range (the gain of input amplifier of the card being 1). If the input signals are in the mV range and the gain of the amplifier is for example 500, then the resultant accuracy of a single measurement is effectively decreased to about 9- or 8-bits only. This decrease in precision is due mainly to the influence of the noise from the digital circuits and the switching power supply of the PC. The specifications provided with XT, AT, etc. buses usually do not provide information on parameters relevant to the effect of electromagnetic noise and interferences on low level analog circuitry inside the computer enclosure. Therefore, new standards for test and measurement procedures such as those available with the VXI bus[99] ("VME bus Extensions for Instrumentation"), and which standardize the mutual influence of the digital and analog circuitry, should play an important role in further improvements of computerized instrumentation. For linking any IBM PC/AT or compatible PC directly to VXI bus system, the VXI-AT2000 device from National Instruments[2] can be used.

The main part of the instrument systems should be designed to enable the possibility of calibration by an operator or autocalibration by a computer program. In this way, circuits can be set in a competent manner within set specifications or the autocalibration program can access a calibration table (a table of offsets and gain errors for different ranges) which is used for recalculation of results so that they are relevant to the specified accuracy of the circuit used an internal standard.

A new possibility in the sphere of data acquisition is the use of A/D converters with an autocalibration function on the chip, e.g. the 12-bit converter SDA 0812 from Siemens[25], the 16-bit converters ADC 4201, 4202, and 4203 from Analogic[59], the 12-bit converters CS5012, CSZ5412, (the CSZ5412 may attain a throughput rate of up to 1 MHz), 14-bit CS5014 and 16-bit CS5016 from Crystal Semiconductor[100], the 12-bit converter with four-channel multiplexer ADC7802 from Burr–Brown[7], the 16-bit converter MN6400 from Micro Networks[101] and other converters from: Catalyst, Texas Instruments, National/TRW[102]. However, a general problem with all these kinds of systems is how to achieve not only static but also dynamic accuracy in order to achieve a desired transfer rate and accuracy at a particular input frequency[103].

5. COMMERCIALLY AVAILABLE SOFTWARE FOR VOLTAMMETRIC INSTRUMENTATION

Despite the fact that software products for instrument control, data acquisition and analysis are widely available for personal computers, selecting the proper software for a particular application is still difficult. The commercially available products span a broad range of functionality, from low-level device drivers to complete high-level development systems and integrated packages. Device drivers are referred to as *The First Generation of Software* because they are the lowest level of software that a programmer can use to control instruments and acquire data without having to have extensive knowledge concerning the hardware interface. Higher levels of software products have tools that aid a user in developing complete application programs. These software packages usually will include facilities for not only aiding data collection but also data reduction, data analysis, and data presentation. Each step *a*) to *c*) presented below represents one or more of the tasks which can be supported by commercially available software:

a) *Data Capture and Control* → GPIB, RS-232, RS-422, Plug-In Boards (Analog, Digital, Counters/Timers), Modular Instruments, Manual Entry;

b) *Data Analysis and Formatting* → Signal Processing, Statistics, PID (Proportional-Integral-Differential) Loops, Curve Fitting, Simulation, Formatting;

c) *Data Presentation and Management* → Graphics, Multi Plots, File I/O, Displays, Data Logging.

The Second Generation of Software builds upon device drivers and creates a higher-level shell. Within this higher-level shell, the programmer uses one consistent development method for combining all of the functions needed to create the application program. The final program is essentially a modified form of the shell, customized to fit the given application.

Several variations to the application shell approach can be used. One approach is to enhance a traditional high-level programming language, such as BASIC, PASCAL or C. Data acquisition, analysis, and presentation functions are added to the language in the form of libraries. The use of standard languages gives the programmer access to a large selection of existing routines written for these languages. Then these source programs can be easily compiled for use as stand alone executable programs. A product of this type is LabWindow. The Siemens PCI-program and a group of related programs (PCI-Generator Genesys, PCI-SNAP, PCI-Panelkit, PCI-Window, etc.) are somewhere between second and third generation software (see below).

Another second generation software approach is to modify a standard language by incorporating data acquisition capabilities directly into the language. The new keywords are built directly into the language as in HT BASIC, ASYST, etc.

Some programs are spreadsheet-orientated software products specially designed for scientific applications (e.g. the Parameter Manager Plus which is instrumentation software for the Macintosh computer) or which add acquisition routines to a Lotus 1-2-3 or Symphony spreadsheet (e.g. the Measure program). Yet another second generation software program category provides menus to access fill-in-the-blank worksheet screens and thus to complete the whole procedure (e.g. the Labtech Notebook program).

The Third Generation of Software builds up software units for construction of Virtual Instruments (VIs) and thus can be used to emulate the functions of the real-world laboratory instruments like signal function generators, digital multimeters, spectrum analyzers, lock-in amplifiers, counters/timers, power supplies, digitizing scopes, digital plotters, etc. A VI can be operated interactively from its own graphical front panel or graphically connected to other VIs to be operated programmatically. VIs are combined to form a whole application program by graphically wiring them together in the same manner that a test setup is built by cabling together individuals physical instruments. The best known example of this third generation program probably is LabVIEW[2] which is for use with 32-bit computers only (e.g., PC AT386 and AT486 with MS Windows, the SUN, the Macintosh, the VAX, etc.).

The LabWindow[2] program (primary version with simplified graphics for 16-bit XT/AT286 and later with full graphics for 32-bit AT386 and AT486 computers, programmable in C language and BASIC) computers is derived from LabVIEW (see the LabVIEW application below). The Virtual Instrument Developer Toolkit for the LabWindow package provides C-language extensions that add predefined user-interface objects to a programmer's repertoire. These objects include controls (pushbuttons, rocker and thumbweel switches, and text-entry windows) and readouts (digital numeric displays, simulated LEDs, and waveform displays) that simulate the controls and readouts generally found on the front panels of real instruments.

The variety and complexity of data acquisition and analysis software now available for personal computers can make the selection of the proper software for a particular application difficult. There are three major factors which need to be considered when selecting a suitable program: ease of use, adaptability and processing speed. Existing programs produce a broad spectrum of possibilities.

Ease of Use. On one end of the spectrum are the "simple" programs which require minimum study before use. On the other end of the spectrum are the "difficult" systems which require much programming and setting of parameters, etc. before they can be used for a chosen task.

Adaptability. "Rigid" systems are designed to do one thing and their function cannot be simply modified. On the other hand "flexible" systems provide programming aids which allow for variable requirements.

Processing Speed. This can mean several things from "slow" to "fast", e.g. how fast the system acquires, stores, analyzes or displays data, or performs control functions (decisions in real time).

Complicated systems which include large amounts of error checking and possibilities for handling many diverse applications obviously must be slower than simple single purpose systems. However, flexible systems sometimes include the possibility of changing program parts so that some error checking, testing and branching of programs can be omitted in order to simplify control algorithms, etc. and thereby achieve a higher speed of operation.

Finally, two other groups of software are mentioned briefly:

a) selected programs for data handling, calculations or simulations, and

b) programs for graphical presentations of experimental results.

The basic building blocks need to be analyzed and understood for proper use of all software programs. These blocks are located at distinctly different levels as described below.

Software drivers (interface routines for communication of the system with the electrochemical hardware) are at the bottom level of the software model. The implementation of these routines has a profound impact on the overall speed and performance of the system. The best source of software drivers for a piece of hardware is usually the supplier of that hardware.

The layer of software above the drivers is the filter layer. These software routines format the raw data coming from drivers and also format data used with drivers from higher software levels. In this level of software there are routines for data conversion, memory management and graphics.

The layer which lies directly above the filter is the language interface layer. On this level there are routines which provide an entry point into the lower system levels (inner system) from the higher level which is programmed in a language such as C, PASCAL or BASIC and vice versa.

The highest layer, which lies directly above the language interface layer is the user interface layer. Different routines for windows, menus, data processing in numeric and graphic forms, etc. are present at this level as well as some user procedures.

The existence of the layered structure makes the system easier to program and more functional, but it also restricts the system's versatility and slows down its execution speed.

Lying on top of the many level system model could be a fifth level where batch files (e.g. *.BAT) or files for changing the computer system configuration (e.g. CONFIG.SYS), etc. are found.

5.1. *Drivers, Special Utility Programs*

Procedures of data acquisition and control cards also usually supply software drivers for their products. These drivers which are programmed in assembler, can be called from the instrument programs as subroutines and linked together with particular programs.

Several firms have modified the BASIC language and added special commands for data acquisition and control, e.g. MBC-BASIC (from MetraByte), HT BASIC (from National Instruments), PCI-BASIC (from Siemens), Soft500 and Quick500 (from Keithley).

Programs from Quinn–Curtis[104] represent examples of the type of general scientific and engineering measurement, real-time graphics, and control tools that may be used.

Examples of typical software packages of drivers and special utilities provided by different firms for their hardware include LAB I/O, PC-LabDAS, Streamer, CODAS, RTMDS, SNAPSHOT STORAGE SCOPE and SNAP-SERIES, and Uncle Scope.

Sometimes drivers or more complicated programs can be prepared with the aid of special development programs, such as Analog Connection Development Systems, PCI-Generator GENESYS[25], LabVIEW and LabWindow[2], DAXpert (for DOS) and GENIE (for MS Windows)[44].

5.2. *Integrated Programs for Data Acquisition, Control, Data Handling, Data Analysis and Graphics*

Programs which support this group of instrument functions are sold by many different companies in the price range of roughly USD 500 to USD 3 000. Obviously, these programs can be used to prepare design of experiment, process control and data handling routines, etc. Final data can be transferred to other programs or saved on a hard disk, or diskettes, etc. in selected formats. Additionally, data from many other programs can be delivered into these programs for data handling and graphical presentation, etc. Powerful software systems of this kind support the contention of one of National Instruments' slogans: "The software is the Instrument". Specific examples of integrated programs are given below.

Labtech Notebook

This product from Laboratory Technologies[105] is a general software package which can be used for multichannel data acquisition, process control monitoring and data analysis. It is compatible with other software packages such as Lotus 1-2-3, Symphony, NWAStatpak, RS/1, DADiSP, MathCAD, etc. The program also allows graphical presentation of measured signals, data transformations, thermocouple based data linearisations and compensations, different modes of feed back control (ON/OFF, PID, etc.), advanced nonlinear function approximations of input data (up to 10 parameters and 10 independent variables), Fast Fourier Transform (FFT), continuous writing of data to the disk during data acquisition and control, and real-time graphic display of data. With the Labtech Real

Time Access optional program, data acquired from the "background" experiment are pipelined directly to the "foreground" program.

The Labtech Notebook software package includes a programming function for those who wish to customize or automate repetitive data acquisition, process control or graph-generating procedures. This option uses MAGIC/L, an incremental compiler language, included in Notebook.

The Labtech Notebook program is supplied on three 360 KB diskettes (Master Disk, Supplemental Disk and Driver Disk). It needs about 512 KB or more memory and is compatible with 8087 or 80X87 numeric coprocessors.

Labtech Acquire is a simple and inexpensive data acquisition system for laboratory use. It is upward compatible to Labtech Notebook.

LT/Control

The program LT/Control from Laboratory Technologies[105] is an example of powerful control software which could be used usefully with on line voltammetric monitoring programs in industry. This system performs trend calculations, process and alarm/limit monitoring and control, data logging and storage on over 500 variables. Real-time display and operator interface and on-line analysis or manual and automatic tuning of control functions can be used. This program runs monitoring and control functions in the background mode while running spreadsheets and analysis programs in the foreground. Real-time data can be communicated between LT/Control and other programs with Real Time Access. The program is upwardly compatible with Labtech Notebook and needs 640 KB of memory.

ASYST, Easyest, VIEWDAC

The program ASYST from Asyst Software Technology[106] is an integrated software system designed exclusively for scientists and engineers but has not been widely used in the construction of electrochemical instrumentation. The ASYST offers instrument interfacing via IEEE-488/GPIB and RS-232, A/D, D/A and digital I/O data acquisition, a full range of scientific analysis and computing capabilities and graphics.

The ASYST consists of four modules:

Module 1. The system, statistics and graphics functions.

Module 2. Analysis – polynomial mathematics, vectors and matrices, regression and frequency analysis, data smoothing, differentiation and integration, peak detection, convolutions and filtering, etc.

Module 3. Data acquisition – analog and digital I/O, real-time synchronization, background data acquisition, array handling functions, graphics, programming functions, etc.

Module 4. IEEE-488/GPIB interface.

Many data acquisitions boards and GPIB boards also are supported. ASYST must have 512 KB of memory (640 KB recommended) and 8087, or 80X87 numeric coprocessors must be installed in the computer. ASYST is prepared in the Meta-Forth language.

For interactive, automatic testing and applications, the new Easyest program can be used. This integrated package with high level tools for A/D acquisition (but Easyest does not support the GPIB or RS-232 interfaces), D/A conversion, analysis and display was written almost entirely in ASYST. Easyest needs an IBM PC/XT/AT type system (including PS/2 and 386- and 486-based computers) with 640 KB RAM, EGA or VGA graphics board, colour monitor and numeric coprocessor.

For 386- and 486-based computers, a new data acquisition, process control, lab automation, real time analysis and graphics software package called VIEWDAC is available. It manages huge data arrays, runs multiple applications concurrently, uses control functions on the screen and self-explaining windows. The package needs a well-equipped PC system that has at least 4 MB of RAM, a numeric coprocessor, 10 MB of free space on its hard disk and a display that conforms to EGA or VGA standards.

ASYSTANT PLUS

The ASYSTANT PLUS is a menu-driven version of the ASYST software package from Asyst Software Technologies[106]. This product is suitable for broad spectrum of applications, but requires no programming or computer expertise. It also needs a numeric coprocessor and at least 512 KB memory as does ASYST. The program version ASYSTANT (also named The Scientific Number Cruncher) has no data acquisition module which is in the ASYSTANT PLUS (which is called by analogy The Scientific Number Cruncher with A/D and D/A Acquisition). Another version of this package is ASYSTANT GPIB (The Scientific Number Cruncher with IEEE-488 Support). This program has modules for many different IEEE-488/GPIB boards instead of modules for A/D and D/A data acquisition boards which are present in the ASYSTANT PLUS. No versions of the ASYSTANT provide for RS-232 interfacing or DMA operation. The ASYSTANT, ASYSTANT GPIB, or ASYSTANT PLUS are provided on four, five or six 360 KB diskettes.

Measure

Measure (former version was Lotus Measure) from Lotus Development Corp.[107] may be used to collect data from instruments and store the information directly in a Lotus' 1-2-3 or Symphony spreadsheet for analysis, storage and display. This program was designed specially for engineers and scientists who work with 1-2-3 or Symphony and has been used to develop computerized electrochemical instruments in our laboratories.

Measure supports three different hardware environments – the IEEE-488/GPIB, RS-232 interfaces, and A/D interfaces from plug-in data acquisition boards. Measure automates applications by the use of advanced macro commands with existing 1-2-3 or Symphony macro commands. This program needs at least 512 KB of memory.

Analog Connection PC

This general purpose data acquisition, control, logging and display program is from Strawberry Tree[45]. It consists of completely menu driven software which does not require any additional programming. The program is written in interpreted BASIC for Strawberry's Analog Connection data acquisition boards and needs only 256 KB of memory.

Controlspread

This spreadsheet look-alike package is provided by SONFAT[46] for their data acquisition board (DAC-12). The program contains extensive control and mathematical functions for direct data acquisition, analysis control and has powerful graphics and display.

DATAWORKS-LS

This program from SONFAT[46] is a menu driven real-time data acquisition and control system provided for the firm's data acquisition board (DAC-12) and can be used for low speed applications. DATAWORKS-LS enables real-time graphs, plots and PID (Proportional-Integral-Differential) control, etc. to be achieved.

PCI-Program Family

The PCI (PC-based Instrument) Software package family from Siemens[25] consists of several programs: PCI-SNAP, PCI-Windows, PCI-Panelkit, PCI-DIF, PCI-BASIC, and PCI-Generator GENESYS.

These programs use the advantages of the software window techniques initially produced for the GEM (Graphic Environment Manager) programming system.

PCI-SNAP (SigNal Analysis Program) is a signal post-processing program which can be completely integrated with existing operator control and display software. PCI-SNAP permits 100 functions to be operated with a mouse and allows windowing, pull-down menus and graphic symbols to be used. This software package is oriented to the needs of instrumentation engineers.

Data obtained from PC-based instrument are converted into DIF (Data Interchange Format) by the PCI-DIF driver program, and allows other programs such as Lotus 1-2-3 to be used to analyze the data. The measured data to be processed can equally well be provided from a stand-alone IEEE-488/GPIB bus device. The PCI-Panelkit program incorporates all IEEE-488/GPIB bus compatible instruments into the PC-instrument system. The PCI-Panelkit helps to produce the exactly required operator interface and presents it graphically on a screen of the monitor because the new instruments are then recognized by the PCI-Windows and the PCI-Generator.

A complete program, from measurement to documentation, can be developed by use of the PCI-Generator program without any programming knowledge. To use an instrument, the pictograph(icon) for the required instrument is simply located on the video monitor screen and then selected, after which the appropriate control mask required to control the instrument appears on the video monitor. The measuring routine can be generated and stored as an autonomous BASIC program by the PCI-Generator program. The source BASIC program can be compiled by a PCI-BASIC Compiler.

Laboratory Workbench

The program Laboratory Workbench from Concurrent Computer[108] is an object-oriented, icon-based software package that simplifies the setting up and controlling of high-performance data acquisition modules and real-time Unix signal processing computers. By constructing simple data-flow diagrams, real-time application programs that control computer devices, data acquisition modules, and graphics subsystems are set up in minutes. This program can be extended with the additional user module, allowing the creation of a library of functions.

Signalys

The Integrated Software Package "Signalys" from Ziegler-Instruments[47] controls all stages of an experiment: data acquisition, data conditioning, data selection, data analysis, data presentation, and graphic display. "Signalys" provides compatibility with data acquisition cards from many manufacturers and can communicate with other programs such as ILS-ASCII and ASYST on the basis of many data file formats.

DAPview

DAPview is an interactive software program for data acquisition and control from Microstar Laboratories[54]. DAPview Plus is a completely integrated system for data acquisition and control and provides support for all common graphic boards as well as a text editor, an on-line help reference manual and error handling facilities, graphics scrolling and crosshair, etc. Its configurations and commands can be saved on disk for complete turnkey applications.

Spurt

Spurt combines the features of data loggers, programmable controllers and closed loop PID controllers in one easy to use integrated package designed for laboratories and pilot plant applications. This program is from Easy Control[109] and it has drivers for PC-Lab cards from Advantech[44] and for the SAPI-86 card family from Tesla Strašnice[75].

5.3. *General Programs for Data Handling and Calculation*

Programs from this diverse software group are used in many laboratories for processing of experimental data and signals. The input information (e.g., experimental data) are entered into these programs manually or loaded as data files with the proper format. In many cases programs of the kind summarized below allow powerful graphical presentations to be made of experimentally collected data but at the same time also allow signal and output data files to be used in a wide range of other programs.

DADiSP

DADiSP 3.0, DADiSP/PRO, etc. (Data Acquisition and Digital Signal Processing) from DSP Development Corp.[110] are a complete graphics-driven post acquisition, data analysis software package designed for scientists and engineers. As a stand alone program, DADiSP provides for very flexible analysis of data both graphically and numerically with the power and flexibility of a spreadsheet. Therefore, this program is also named the Technical Spreadsheet.

DADiSP offers more than 160 different analysis routines including arithmetic, calculus, waveform generation, Fourier analysis, frequency domain analysis, correlations, trigonometric and statistical. Complex numbers and engineering units conversion are also supported.

PIPELINE boosts the power of DADiSP substantially by allowing external programs (e.g. third-party data acquisition and plotter drivers as well as analysis and filtering algorithms to process the data, etc.) to be executed directly from within the DADiSP environment.

DADiSP can analyze and display up to 64 windows and up to 9 windows can be displayed on the screen at the same time. Some experimental data can be recorded with the PROTOCOL set up and DATASET. A separate disk-based program module DADiSP-488 establishes a direct link to IEEE-488 instruments.

Programs Analogous to DADiSP

A much simpler program than DADiSP for a control and analysis is the program MEDUSA III/MIRACEL from Innovative Elektroniksysteme[111]. It uses four windows to display and handle data and several fundamental mathematical functions and algorithms for data processing.

The program package PC Data Master from Durham Technical Images[112] includes over 50 files (approximately 1 MB of executable code) of DSP and graphics utilities which are called from the shell. The enhanced DOS environment has powerful and flexible capabilities for data processing and display.

The Enhanced Graphics Acquisition and Analysis (EGAA) software from R.C. Electronics[113] is a multi-tasking program for test and measurement applications. Up to 8 different tasks can be operated concurrently and the master controller of the EGAA system – the System Executive – automatically links data acquisition, data conditioning, event detection, and analysis tasks. Defined tasks can be viewed simultaneously. The EGAA collaborates with the companies data acquisition hardware

ISC-16, while the general purpose data acquisition and data processing programs used are PH/LAB from MediWare[114] and DiSys software package for control systems from MERLIN[115], respectively.

RS/1

The RS/1 program package from BBN Software Products[116] has become an industry standard in general data analysis software. It consists of a data management, a range of data analysis tools, statistics, presentation graphics, curve-fitting, etc. This package needs a hard-disk and 512 KB of memory.

Examples of Programs for Calculation, Statistics and Graphical Presentation

A list of selected general programs for calculation, statistics, and text or graphical output on the screen, plotter or printer follows. These programs can be used for different tasks such as experimental data handling, preparation of new input parameters of planned experiments, etc.: MathCAD from MathSoft[117]; Eureka from Borland[118]; TK Solver Plus from Universal Technical Systems[119]; Gauss from Aptech Systems[120]; Reduce from Rand Corp.[121]; Derive (A Mathematical Assistant) from Soft Warehouse[122]; The Scientific Desk from C. Abaci[123]; IMSL (Libraries MATH, STAT, SFUN) from IMSL[124]; NAG's PC50 Library from Numerical Algorithms Group[125]; MATLAB from Math Works[126]; Mathematica from Wolfram Research[127]; MAPLE from Waterloo Maple Software[128]; Other mathematical software packages are discussed in ref.[129], etc.: Axum from TriMetrix[130]; Sigma-Plot from Jandel[131]; Statgraphics from STSC[132]; Sigstat from Significant Statistics[133]; Systat and Sygraph from Systat[134]; Dyna-Stat from Dynamic Microsystems[135]; CSS from StatSoft[136]; BMDP/PC, BMDP EP/286, BMDP/386 from BMDP Statistical Software[137].

Programs for Simulation of Electrical Circuits

Several CAE programs useful for solving special tasks in electrochemistry (e.g., AC voltammetry, modeling of a double-layer) or in electrochemical instrumentation are listed below. These programs simulate both analog and digital types of circuits and thus some models represented by networks of electrical elements such as R, L, C, transformer, diode, transistor, operational amplifier, digital logic circuit, etc., can be solved and verified: PSpice and the Design Center from MicroSim[138]; Micro-Cap and Micro-Logic from Spectrum Software[139]; TUTSIM from SONFAT[46]; SADYS from ČVUT FEL, Praha[140]; COCO SN from VUT FEL, Brno[141]; IS SPICE or as a package ICAP/2 from INTUSOFT[142]; PACSIM from Simucad[143]; ECA-2 from Those Engineers[144]; ENAP from EMONA Instruments[145].

These programs are obviously interactive electronic drawing and analysis programs that allow fast simulations on networks. They perform AC, DC, transient, FFT, Monte Carlo, etc. analyses and results are displayed or plotted.

Program COCO SN (Cofactor Computation) expresses algebraic cofactors of a network admittance matrix in a polynomial form.

Presentation Graphics Software

Many different programs are used for engineering and scientific graphical presentation of experimental results. Some of them are listed below: Tech*Graph*Pad from Binary Engineering[146]; Fig.P from BIOSOFT[147]; SlideWrite Plus from Advanced Graphics Software[148]; Chart from Microsoft[149]; Easy-Plot from Spiral Software's programs which is distributed by Cherwell Scientific[150].

Other programs are available for special tasks as curve-fitting, e.g. ENZFITTER from BIOSOFT[147] or DIFFEQ from MicroMath Scientific Software[151], which provides flow chart presentation of experimental procedures, etc.

6. EXAMPLES OF INTERFACES USED IN VOLTAMMETRIC INSTRUMENTATION

In 1981, we commenced construction of a universal electrochemical workstation named the Electrochemical System[152] using a mixture of approaches described in this article. The design of the Electrochemical Interface 1 (EI 1) was undertaken at Deakin University, Australia in the years 1981 – 82. This task was based on collaboration of staff from Deakin University, Geelong, Australia and The J. Heyrovský Institute, Prague, The Czech Republic. Coworkers H. B. Greenhil and F. L. Walter from Deakin University participated in the system design and this research project was supported by Deakin University, the Australian Research Grants Scheme and The J. Heyrovský Institute. Construction of this EI 1 was finished at The J. Heyrovský Institute in 1983 together with software called the Chemical Program Package (CPP) for three dimensional (potential–current–time) electrochemical measurements[153], FFT, and graphical presentation, etc. That is, in the early 1980s it took us about 2 years to fully develop a computerized electroanalytical system for undertaking voltammetric measurements. Since this time, we have built several much more powerful systems in 6 month periods with the aid of some of the more recent software packages described in this article.

EI 1 was designed with a Tandy TRS-80 microcomputer. This microcomputer with Z80 microprocessor was popular in Australia in the early 1980s where it was commonly provided by Tandy and Dick Smith Electronics, and also in Czechoslovakia where the Z80 microprocessor was used in a cloned form from several manufacturers under names such as Video Genie EG (from Hong-Kong), Mikro ZK 88 (from Vývojové dílny ČSAV), EG-MON (from the MON organization), etc.

Our aim in the early 1980s was to design an Electrochemical System (ES) for automation of electrochemical experiments, and to provide extensive capabilities for data handling, graphics, development and debugging of new programs and hardware, programming EPROMs, etc. which is comparable with the performance of most of the current commercially available instruments.

The electrochemical system, ES, (Fig. 4) shows the keyboard with the main part of the microcomputer (CPU), the Expansion Interface, the Video Display, the three minifloppy disks 5.25 inches, the Consul 2111 printer, the FS 1503 punchtape reader, the Robotron 5-3297 puncher, the BAK 5T X-Y recorder, the Tesla BM-463 oscilloscope, the EPROM eraser, the EPROM programmer[154], the Electrochemical Interface EI 1, and the electrochemical working place where the static mercury drop electrode SMDE 1, the classical dropping mercury electrode with a hammer for mechanically detaching mercury drops and the three electrode electrochemical cell, etc. are situated. The EI 1 is connected to the Expansion Interface of the TRS-80 system via its inner data and address buses and control lines. This EI 1 contains the following function blocks:

a) A power supply.

b) A Zero-crossing detector circuit which generates a 50 Hz signal in phase with the mains frequency and also a Phase Lock Loop (using a CD 4046 device for multiplying of the instant mains frequency by 128 or 256 so that measurements can be made 128- or 256-times during the mains period, thereby emulating an integrating type of A/D conversion).

c) Control and Decoding Logic.

d) Parallel I/O (48 buffered lines – TTL levels).

e) A serial I/O (RS 232C).

f) A timing/counting circuit.

g) A 2 KB EPROM for control and conversion subroutines.

h) A potentiostat with a 3 electrode configuration (max. ±13 V, ±200 mA).

i) A current-to-voltage converter with 10 ranges from ±20 nA to ±5.243 mA FS. (The ranges may be set manually or from the computer program).

j) Three 12-bit D/A converters for (i) background current compensation on the I/E converter input; (ii) driving of the potentiostat with a DC ramp and the possibility of superimposed pulse or digital AC signals; (iii) X–Y recorder control.

k) A sample and hold circuit and a 12-bit A/D converter.

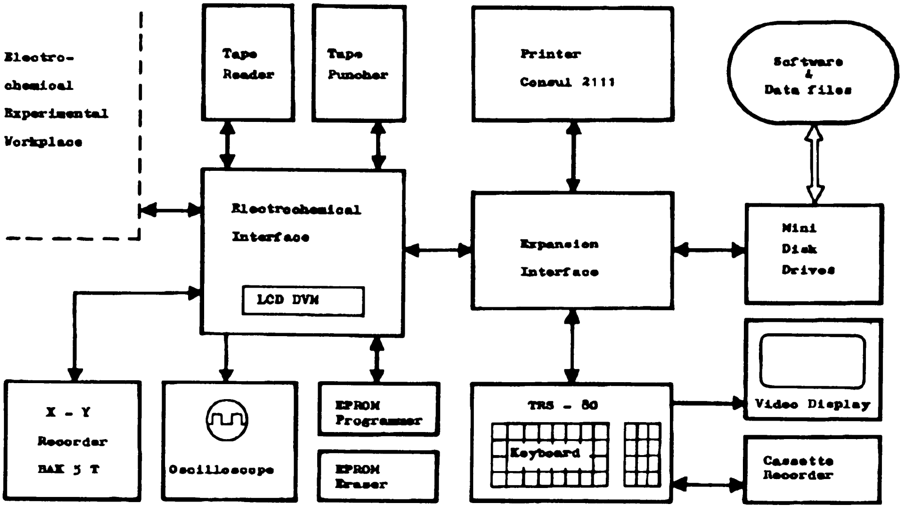


FIG. 4

Block diagram of the first Electrochemical System built in our laboratories (see text for details) *l*) A 3 1/2 digit LCD digital voltmeter for two ranges: ±199.9 and ±1 999 mV.

An Electrochemical Interface 2 (designed in The J. Heyrovský Institute) was based on the EI 1 design but expanded to include a galvanostat and also contained several improved optical bar and digital LED displays. A more recent Electrochemical Interface 3 using a PC of the IBM PC/XT/AT type with an Advantech PCL-718 card for data acquisition and control and separated analog part with power supply, indications (displays, LEDs, etc.), potentiostat/galvanostat, I/E converter, *IR* compensation, combined dummy-cell, etc. has been fabricated as a further extension of the previous EI 1 and EI 2 systems.

Many different versions of computerized electrochemical (voltammetric and ionselective electrode) systems have been designed at Deakin University during the 1980s utilizing different microprocessor chips and microcomputer systems and software support systems (see refs[155 - 181] for examples and applications). The systems have been used in fundamental investigations of electrode mechanisms as well as in applied projects involving on-line monitoring of industrial processes where some degree of intelligence has been incorporated. Of particular interest is the recent development of completely battery operated computerized systems (see refs[164,168,169,175,176]). With the advent of low powered CMOS (complementary metal oxide semiconductor) devices, all circuits relevant to electrochemical type instrumentation are now available in battery powered versions. Hence, the possibility of fully automated and computerized systems is therefore realizable for field based analytical work. However, the software support and the speed that can be achieved with battery generated computerized instruments is still not as good as with the mains powered devices.

7. EXAMPLES OF ELECTROCHEMICAL INTERFACES BUILT IN OTHER LABORATORIES

The number of microcomputer (microprocessor) based electrochemical interfaces described in the literature is too numerous to review comprehensively. Rather, we have selected a few representative examples to illustrate the range of computerized concepts introduced and the almost universal geographic spread of the countries from which the contributions have originated.

In a review of digital computers in electrochemistry, He and Faulkner[182] identified six roles for digital computing in electrochemistry:

(*a*) sample preparation;

(*b*) experimental control;

(*c*) preparation of data for interpretation;

(*d*) model building (the prediction of electrochemical response by theory, e.g. digital simulation);

(*e*) interpretation (comparison of results with the theoretical model);

(*f*) tactical and strategic decision making.

In the broad sense each of these areas refer in some way to what may be termed computer aided electrochemistry and applications encompassing one or more of the six areas where electrochemistry may be aided are now also widely available, unlike the situation in 1988 where categories (*a*) and (*f*) in the He and Faulkner review could not be represented by large numbers of examples. In the last few years, these two gaps have begun to be filled. The need for on-line monitoring has led to systems containing automated sampling features and chemical or mathematical treatment to remove interference as perusal of refs[174,176,178,180,183 - 186] will indicate. Similarly, in the area (*f*) of the He and Faulkner classification, the development of a knowledge based system for elucidation of electrode mechanisms[187], an expert system for pharmaceutical analysis[188], applications of chemometrics[189 - 191] and the development of intelligent and automatic compensation of solution resistance[192] represent examples to demonstrate the rapid expansion taking place in this category. However, it is still true that the majority of papers applying computers to electrochemical problems are broadly defined as those covering areas (*b*) and (*c*).

A large number of papers related to microcomputer based instrumentation, as would be expected, concern the development of electrochemical interfaces (data acquisition systems) which can be coupled to commercially available instruments to improve their versatility, extent of automation, etc. These encompass categories (*b*) and (*c*) in the He and Faulkner classification. For example, several authors have discussed interfaces which control the PAR Model 273 electrochemical instrument[193,194] and other digital and analog instruments made by PAR (EG & G Princeton Applied Research Corporation) including the PAR Model 173/178 type combinations[195,196], Model 174A[198], 384A and 384B Polarographic Analyzers[197 - 200] and the PAR Model 170 Electrochemistry System[201].

Related interfaces have been reported for converting the analog Metrohm E506 Polarocord and BAS (Bioanalytical Systems)[202] CV-27 potentiostat into digital electrochemistry systems[203], and indeed, many other equivalent systems. Discussions of electrochemical interfaces not as confined in scope are contained, for example, in refs[204 - 232]. These electrochemical interfaces have been applied to almost every conceivable type of electrochemical equipment. Specific applications, such as the field determination of heavy metal by a battery operated digital system[233,234], the on-line shipboard determination of trace metals in sea water[235] and facilitation of studies on brain chemistry[236] complement the more general papers which emphasise the enhancement of the electrochemical techniques by the use of digital methodology[203 - 232]. Categories (*d*) and (*e*) in the He and Faulkner classification, are outside the scope of this article, but have also been drastically expanded in the last 10 years.

References cited in this section have not necessarily utilized the advanced software systems available and cited in this review. However, recent papers by David and Papadopoulos[237] and Mannino et al.[238] are worth citing at length to illustrate how simply computerized electrochemical instrumentation may be designed with areas to appropriate hardware and software packages.

In the paper by David and Papadopoulos[237] a potentiostat and a drop knocker were interfaced to a Macintosh computer, using LabVIEW for the programming of the interface. The whole system performs the function of a pulse polarograph and digital storage of the experimental data permits baseline subtraction and digital filtering of the experiment.

The philosophy behind the development of the pulse polarograph, as stated in ref.[237], really summarises the theme of the present article and is reproduced in part below to provide an alternative expression of likely developments in electrochemical instrumentation in the 1990's.

David and Papadopoulos summarise difficulties encountered in the last decade in the following terms.

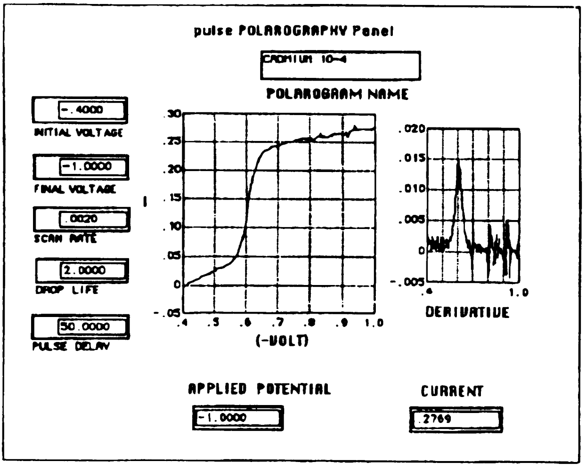
"The new generation of microcomputers permits the use of a high level language (for example, compiled BASIC, PASCAL, or C), which can shorten development time for writing an application program considerably. However, to produce an integrated data acquisition, analysis, and presentation solution, very complex software is usually needed. A basic program for instrument control, acquisition analysis, and presentation of the data appears as many pages of long subroutines called by a central subroutine whose calling statements do not really explain the relationship between the call functions. In addition, software documentation is time consuming and often is virtually nonexistent, making code reuse impractical."

They then discuss the use of LabVIEW as an aid to developing a polarographic system and demonstrate how this form of software overcomes some of the problems.

"LabVIEW, a software program from National Instruments that permits data flow programming, offers an alternative solution that dramatically shortens programming time. The first step in every software design is the block diagram of the application. With a conventional language, the only use of the block diagram would be to show someone else what the program is supposed to do. With LabVIEW, the block diagram is the actual program, eliminating the need to convert the block diagram to long listings of instructions. A block diagram program is created by choosing graphical elements and writing them together. The manipulation of the graphical items, which consist of the syntactic structures of this graphic language is possible by means of the placement, wiring, operating and labelling tools in the LabVIEW Programming environment. With this software a Virtual Instrument (VI), the basic building block of LabVIEW, can be constructed. The various functions and structures of a conventional programming language (arithmetic, comparative, array manipulation, timing, etc.) are also found in LabVIEW in the form of icons that can be selected from the functions menu. Any computation possible with a conventional language is also possible with LabVIEW. LabVIEW provides an integrated environment for developing and executing an application requiring instrument control, data acquisition and presentation in the form of a virtual instrument. The virtual instrument is a software program that looks and acts like a real world instrument. A real world instrument possesses a front panel with a combination of indicators, knobs, switches and sometimes a strip chart recorder. The VI duplicates the front panel of a classic instrument on a Macintosh screen. The programmer can select from a menu of a variety of knobs, switches, displays, graphs and plots to give the operator a simple, understandable format to interact with the computer. After establishing the inputs and outputs of the application, the block diagram describes the flow of information and control between these points. The elements of the diagram represent sub-programs that are wired into the dataflow between input and output. Elements of the block diagram can be a lower level VI. Each VI has in icon associated with it that represents it in the block diagram of a larger VI. Each icon possesses a set of connecting terminals that define the points of the icon that receive input and provide output. Representative icons can be created by using the icon editor, incorporated in the LabVIEW software package."

Finally, David and Papadopoulos describe the pulse polarograph they built with the aid of LabVIEW to demonstrate what can be done.

"Figure 5 shows the front panel of a pulse polarography VI. The operator is able to select the initial and final potential, the drop time, scan rate and the pulse duration. The potential applied to the cell and the current measured are shown on the front panel during the experiment. At the end of the experiment the *I–V* plot and the first derivative of the *I–V* plot are displayed. Figure 6 shows the block diagram of this instrument. In this block diagram various sub VIs are wired together in the same manner that a measurement setup is built up by cabling together individual physical instruments. The



CROMIUM 10-4
POLAROGRAM NAME

-.4000
INITIAL VOLTAGE

-1.0000
FINAL VOLTAGE

.0020
SCAN RATE

2.0000
DROP LIFE

50.0000
PULSE DELAY

APPLIED POTENTIAL
-1.0000

CURRENT
.2769

FIG. 5
Panel of a computerized pulse polarographic system built with the aid of LabVIEW. Reproduced by courtesy: Electroanalysis 3, 721 (1991)

"logic" VI receives input from the initial voltage, final voltage, scan rate and drop life and provides as output the pulse height and the number of mercury drops needed to complete the experiment. The "time" VI provides the timing. The "*I–V*" VI produces the waveform needed for pulse polarography and measures the current. The "Hammer" VI dislodges the mercury drop at the end of its life. The "plot" VI displays the *I–V* plot and its first derivative on the front panel and the "send to disk" VI opens a file and saves the data on the disk. The "*I–V*", "time" and "hammer" VI are inside a for-next loop. An interesting feature of LabVIEW is that noninterconnected VIs inside a block diagram execute in parallel. With a computer having true parallel processing, two separate instructions can be executed simultaneously. On a single processor computer instructions must execute sequentially. LabVIEW uses a time-sharing mechanism of the CPU time so the user does not have to decide the order of execution arbitrarily, thus simplifying programming.

To interface an analog instrument via LabVIEW to a Macintosh computer, an NB-MIO-16 interface card is necessary, which is supplied by National Instruments. This card contains a 12-bit analog to digital (A/D) converter with 16 analog inputs, two 12-bit digital to analog converters (D/A), 8 lines of TTL comparable digital input output, and three 16-bit counter timers for timing. A/D conversion rate can be up to 100 kHz. LabVIEW provides the software drivers needed to configure and control the various functions of this card in the form of icons. Thus, there is no needed for a great deal of technical knowledge about the hardware. The programmer uses the icon of the hardware driver by incorporating it into the block diagram of a VI. By removing the need to program the details of the hardware the programmer's work is considerably

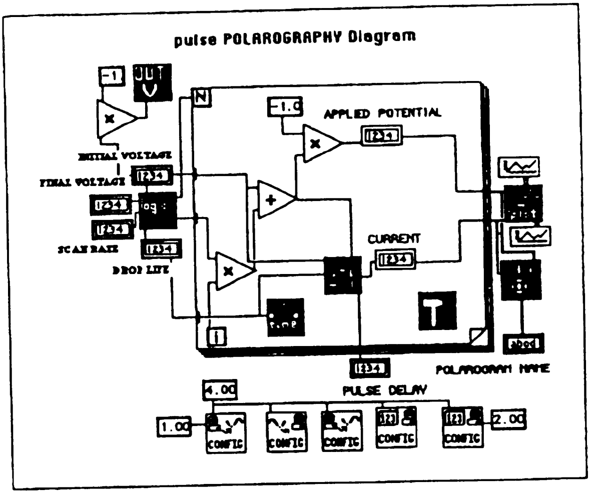


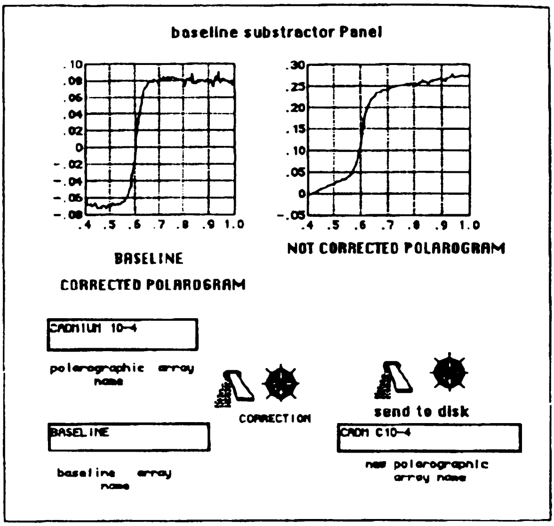
FIG. 6
Block diagram of a pulse polarographic system built with the aid of LabVIEW. Reproduced by courtesy: Electroanalysis 3, 721 (1991)

reduced. In ref.[237] this card was interfaced with a PAR model 373 potentiostat and Tacussel type EGMA polarographic stand.

Figure 7 shows the front panel of a baseline substractor VI. This VI substracts two polarograms saved in the disk. The polarogram name and the baseline name are entered, the baseline is substracted from the polarogram, and the resulting polarogram is saved in the disk under a new file name. Figure 8 depicts the front panel of a filter VI. The polarogram name is entered. The operator changes the filter parameters, and when satisfied with the result, the filtered polarogram may be saved in the disk under a new file name. In the examples shown digital filtering and digital derivation have been performed using icons from the digital signal processing library of LabVIEW."

The second example to be described in some detail concerns the development of a computerized system for potentiometric stripping analysis[238] using a commercially available Radiometer Instrument, Lab Master Components for interfacing and Asyst software (see sections ASYST, Easyest, VIEWDAC and ASYSTANT PLUS above).

To develop a computerized potentiometric stripping instrument, the Radiometer ISS820, which was used only to control the plating potential was simply connected to the daughter board of the Lab Master card through the P1D connector. In turn the Lab Master card communicated with the computer through the mother Lab Master card. Analog/digital conversion was performed using one of the eight true differential channels with 12-bit resolution. The conversion was started with an ASYST software command using the programmable timer AMD 9513 inserted in the Lab Master mother board. An AT IBM-compatible microcomputer (640 K memory) equipped with an 80X87 mathematical coprocessor, enhanced color graphics card, and ASYST software



polarographic array name: CADMIUM 10-4

baseline array name: BASELINE

new polarographic array name: CADM C10-4

FIG. 7
Baseline substraction panel of a computerized pulse polarographic system built with the aid of LabVIEW. Reproduced by courtesy: Electroanalysis 3, 721 (1991)

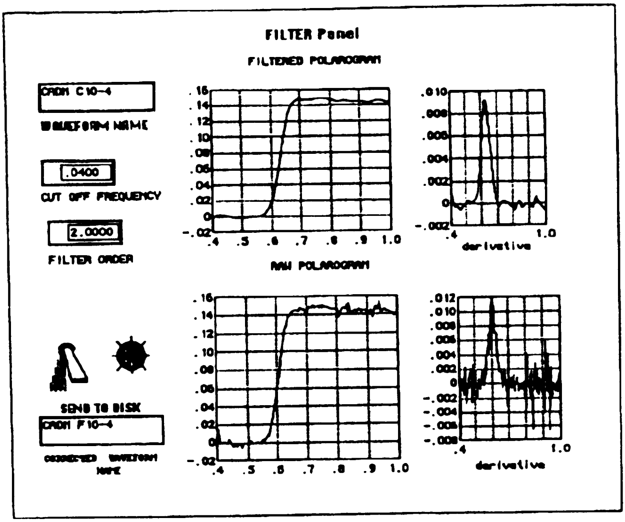
(Version 2.0) was used to collect, process and display data from the potentiometric stripping system. These data were usually plotted on a 7470-HP compatible serial plotter.

In ref.[238] it was noted that ASYST is a scientific programming language that allows one to define and link routines in a very simple way (by using simple words) and the principal advantages noted were the convenience of "top-down" program design, the variety of sophisticated mathematical functions available, and the facility to perform array manipulations and construct an information graphic display.

The application software in this paper devoted to potentiometric stripping analysis (PSA) was developed as a set of task-oriented routines constructed by combining simple ASYST words describing the sequence of operations. The main subroutines used in the program are described in Table I and the details of the most important subroutine, ANAL, used to acquire and elaborate data, are described in Table II.

Background-corrected graphs, as they appear on the screen, obtained by the computerized, PSA, system on a standard solution containing cadmium, lead and copper are presented in Fig. 9 while a potentiogram of lead obtained by analyzing a vinegar sample is shown in Fig. 10.

ASYST proved to be flexible and powerful tool for developing software that has significantly contributed to the development of the PSA computerized system. The application of this system to the determination of lead in wine and vinegar showed that lead determination at the level normally found in these matrices can now be performed without deaerating the sample and with short plating times.



WAVEFORM NAME: CADM C10-4

CUT OFF FREQUENCY: .0400

FILTER ORDER: 2.0000

CORRECTED WAVEFORM NAME: CADM F10-4

FIG. 8

Filter panel of a computerized pulse polarographic system built with the aid of LabVIEW. Reproduced by courtesy: Electroanalysis *3*, 721 (1991)

8. CONCLUSIONS

In the early 1990s it is clear that computerized electrochemical instruments are now readily constructed from commercially available hardware and software. However, despite this, advances achieved by introduction of microprocessors in commercial instruments have been generally disappointing relative to advances achieved in spectroscopic methods. In the 1990s, if voltammetry is to progress or even expand on its role as a modern instrumental method widely used in analytical chemistry then application of expert systems with artificial intelligence must be greatly increased. For example, evolution into the new smart systems in addition to achieving some features described in

TABLE I

Main subroutines of the program available in the computerized potentiometric stripping analysis system developed with the aid of ASYST software and described in ref.[238]

RUN	Initialize Lab Master board and start PSA experiment.
KEPR	Assign features to the functions keys to call the main subroutines.
ANPA	Allow to set all experimental parameters for a PSA experiment.
CYMO	Allow repetitive measurements with identical instrumental parameters.
ANAL	Perform analysis; acquire and elaborate data (differentiate, smoothing and so on).
INDA	Search for peaks; integrate and display results on video.
PLDA	Display potentiograms and results and send them to plotter or printer.
WRFI	Register potentiograms and analysis parameters in computer memory.

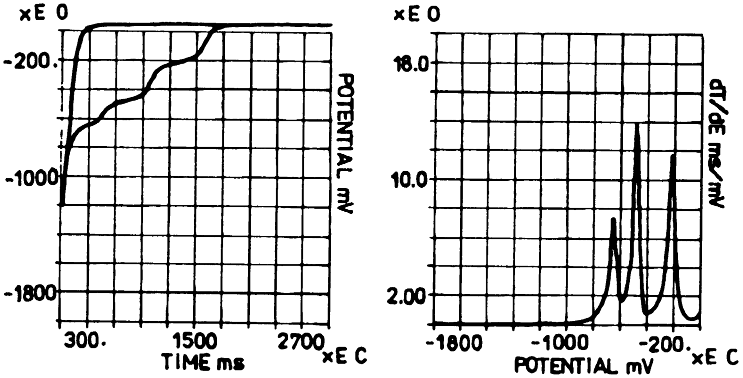


FIG. 9

Potentiometric stripping curves obtained for lead (300 ppb), cadmium (200 ppb) and copper (100 ppb) in 0.1 M HCl using a computerized system built with the aid of ASYST software. Deposition for 1 min at −1.2 V, left hand side (original), right hand side (derivative). Reproduced by courtesy: Electroanalysis *1*, 177 (1989) the Introduction could lead to the elimination of the potentiostat. This is a noisy electronic device and return to a two electrode system with calculation of the cell transfer function and calculation and correction of *IR* drop by software may provide a superior approach for undertaking very high speed experiments and trace analysis applications, provided the reference electrode is not polarized by the current flowing through it. An expert system, with capabilities for organizing and optimizing experiments and their

TABLE II
Details of the subroutine ANAL available in the computerized potentiometric stripping analysis system developed with the aid of ASYST software and described in ref.[238]

(1) Release potential for a chosen time in order to strip metals eventually present in the electrode amalgam.
(2) Set the deposition potential to the desired value and perform electrolysis for the time programmed.
(3) Release potential and acquire data, storing them in a named array.
(4) Display potentiogram (potential vs time) on the video screen.
(5) Perform axes transposition; arrange data array in the form of an histogram (using 2 mV resolution) that can be visualized on the screen as d*t*/d*E* vs potential.
(6) Perform background curve and store data in a named array.
(7) Subtract background array from the primary curve array.
(8) Smooth background corrected curve with a chosen filter cutoff frequency (usually 0.25 cycle/point).
(9) Call subroutine PLDA to visualize potentiogram on the video screen and then INDA and PRDA subroutines to send the potentiogram to the plotter or printer.

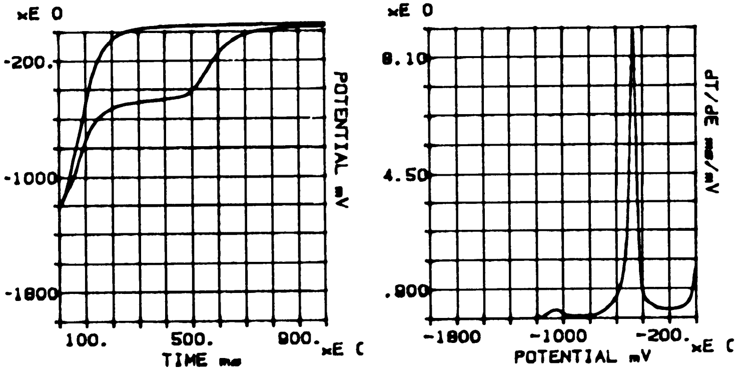


FIG. 10
Potentiometric stripping analysis curves of a vinegar sample with lead, as they appear on the video screen of a computerized system built with the aid of ASYST software: left hand side original; right hand side derivative. Reproduced by courtesy: Electroanalysis *1*, 177 (1989)

design would surely render obsolete the idea that voltammetric experiments should be any longer classified into numerous pulse, square wave and alternating current methods, etc. Application of single DC potential scan, multi-time domain and/or multi-frequency experiments should replace the need for numerous experiments to be employed with single time domain – single frequency domain experiments. For example, it is considered desirable that an FFT electrochemistry system containing equivalent computing and mathematical power to FFT Nuclear Magnetic Resonance experiments will become available commercially.

The ability to apply robotic sample preparation methods, or automated sampling and sample treatment with flow injection techniques with voltammetric detection also need to be introduced with commercially available instrumentation. A need for development of data bases as powerful and extensive as those available in infra-red and mass spectrometry may be essential precursors for the development and use of expert systems. Since voltammetric instrumentation only is associated with current–potential– time (frequency) considerations, the technique is more compatible with computers than almost any other form of chemical instrumentation. For example, the spectroscopic instrument, with the need to interface optical or magnetic rather than purely electronic components, generally needs to be much more complex and expensive than the electrochemical interface. However, perhaps, the greatest inhibition to the development of state-of-the-art electrochemical instrumentation has been the long acclaimed attraction that electrochemical instrumentation is inexpensive. However, ironically, it can be noted that advances that have taken place in other areas of chemical instrumentation mean that for example what may be regarded as very expensive ICP mass spectrometers can now provide 70 or so element determinations from a single experiment with parts per trillion capabilities in many instances but at a cost per individual element that cannot be matched by voltammetric methods addressing the same problem. The problem is that voltammetric methods usually require sequential single element experiments or at best perhaps 2 to 4 simultaneous element determinations from each experiment. Perhaps the smart voltammetric instruments developed in the 1990s will have the good sense to actually recommend the use of ICP-mass spectrometry on economic grounds for some determinations, but recommend the use of voltammetry for specialized applications when voltammetry really is superior to spectroscopic methods?

For studies aimed at elucidating mechanisms and other aspects of redox processes of organic, inorganic, organometallic, biological and biochemical importance, the new generation of electrochemical instrumentation in the 1990s should be very suitable. Packages of digitally simulated electrochemical mechanisms should become available which can be run on the same microcomputers (with parallel processors) that are controlling the equipment so that close to real-time theory–experiment comparisons and real-time conclusions concerning the correctness of a particular redox mechanism should be achievable. Unfortunately, unlike in X-ray crystallography where there are a finite number of space groups, in voltammetry, there are an infinite number of mechanisms so that philosophically it is will probably never be possible to provide the universal mechanistic software package that is available in X-ray crystallography.

In the area of electroanalytical chemistry, ready and efficient achievement of optimal methodology may enable proper focus to be directed onto those areas where electrochemistry may excel even in competition with other methods, e.g. on-line monitoring, battery operated systems applied in remote areas, measurements in living organisms aided by the use of microelectrodes, some areas of HPLC with electrochemical detection where unique and highly sensitive multi-species determinations or other features make voltammetric detection the clear method of choice. In this sense, perhaps it is time that electroanalytical chemists learned to live with the fact that electrode fouling, electrode drift and matrix affects are a fact of life and to build the experience necessary to cope with these problems into an expert system. For example, if the electrode area is partially blocked during continuous on-line use, the smart, intelligent or expert system should know how to compute and correct for the decreased electrode area or changed kinetics or how to polish the electrodes or replace them with new ones if the electrode becomes broken. The alternative of continuing with the dream of building the infinite lifetime, totally reproducible and perfect electrode seems more remote than building an expert system that knows how to recognize and deal with the problem in the same way that we have to manually deal with the problem with today's instruments.

In summary, we predict that the new generation of smart voltammetric instrumentation, which is now technically feasible to build, should find its way into many research laboratories by the end of this century. However, unless the present generation of instrument manufacturers can be persuaded to commercialise such forms of equipment, then it seems that voltammetric methods will continue to fall well behind their theoretical level of performance, since other instrumental methods of analysis already known to be commercially viable will attract all the resources and attention.

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38. ELORG, Moscow, U.S.S.R.
39. Dataq Instruments, Inc., Akron, OH 44311, U.S.A.
40. Boston Technology Pty Ltd., Milsons Point, N.S.W. 2061, Australia.
41. International Business Machines Corp., White Plains, NY 10604, U.S.A.
42. Data Translation, Inc., Marlboro, MA 01752-1192, U.S.A.
43. MetraByte Corp., Taunton, MA 02780, U.S.A.
44. Advantech Co. Ltd., Shing-Tien City, Taipai, Taiwan.
45. Strawberry Tree Computers, Inc., Sunnyvale, CA 94086, U.S.A.
46. SONFAT, Artarmon, N.S.W. 2064, Australia.
47. Ziegler-Instruments GmbH, 4050 Monchengladbach 4, F.R.G.
48. HEC, 5110 Alsdorf, F.R.G.
49. Dalanco Spry., Rochester, NY 14618, U.S.A.
50. Kenda Electronic Systems Ltd., Totton, Southampton SO4 3NB, U.K.
51. Laboratory Software Associates Pty Ltd., Fitzroy, Victoria 3065, Australia.
52. Contect Microelectronics, Inc., San Jose, CA 95131, U.S.A.
53. Computer Boards, Inc., Mansfield, MA 02048, U.S.A.
54. Microstar Laboratories, Redmond, WA 98052, U.S.A.
55. SORCUS Computer GmbH, 6900 Heidelberg, F.R.G.
56. Rapid Systems, Seattle, WA 98103, U.S.A.
57. Soltec Corp., San Fernando, CA 91341, U.S.A.
58. ADAC Corp., Woburn, MA 01801, U.S.A.
59. Analogic Corp., Centennial Industrial Park, Peabody, MA 01961, U.S.A.
60. GaGe, Applied Sciences, Inc., Montreal, Quebec H4S 1S1, Canada.

61. Real Time Devices, Inc., State College, PA 16803, U.S.A.
62. ADDI-DATA GmbH, 7580 Buhl, F.R.G.
63. Blue Chip Technology, Deeside, Clwyd CH5 3PP, U.K.
64. Kolter Electronic, 5042 Erftstadt, F.R.G.
65. Wilke Technology GmbH, 5100 Aachen, F.R.G.
66. Digimetrie, 66000 Perpignan, France.
67. Industrial Computer Source, San Diego, CA 92131, U.S.A.
68. Datel, Inc., Mansfield, MA 02048, U.S.A.
69. TransEra Corp., Provo, UT 84604, U.S.A.
70. Signalysys Ltd., Buckland Village, Bucks HP22 5HU, U.K.
71. AXIOM Technology Corp. Ltd., Hsin Tien, Taiwan.
72. Industrial Computer Source, San Diego, CA 92111, U.S.A.
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75. Tesla Strašnice k.p., 130 00 Prague, The Czech Republic.
76. disys Mess- und Testsysteme GmbH, 51503 Rösrath, F.R.G.
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107. Lotus Development Corp., Cambridge, MA 02142, U.S.A.
108. Concurrent Computer Corp., Westford, MA 01886, U.S.A.
109. Easy Control, 320 04 Plzeň, The Czech Republic.
110. DSP Development Corp., Cambridge, MA 02139, U.S.A.
111. Innovative Elektroniksysteme GmbH, 5000 Köln 41, F.R.G.
112. Durham Technical Images, Durham, NH 03824-0072, U.S.A.
113. R.C. Electronics, Inc., Santa Barbara, CA 93111, U.S.A..
114. MediWare, 9747 AN Groningen, The Netherlands.
115. MERLIN s.r.o., 140 00 Prague, The Czech Republic.
116. BBN Software Products, Cambridge, MA 02238, U.S.A.
117. MathSoft, Inc., Cambridge, MA 02139, U.S.A.
118. Borland International, Inc., Scotts Valley, CA 95066, U.S.A.
119. Universal Technical Systems, Inc., Rockford, IL 61101, U.S.A.
120. Aptech Systems, Inc., Kent, WA 98042, U.S.A.
121. Rand Corp., Santa Monica, CA 90406, U.S.A.
122. The Soft Warehouse, Inc., Honolulu, Hawaii, U.S.A.
123. C. Abaci, Raleigh, NC 27605, U.S.A.
124. IMSL, Houston, TX 77042, U.S.A.
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143. Simucad Corp., Menlo Park, CA 94024, U.S.A.
144. Those Engineers Ltd., West Hampstead, London NW6 1DS, U.K.
145. EMONA Instruments, Camperdown, N.S.W. 2050, Australia.
146. Binary Engineering, Waltham, MA 02154, U.S.A.
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