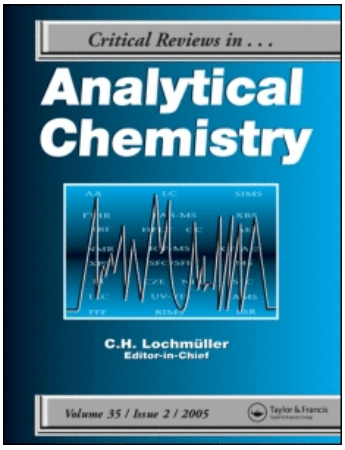

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AUTOMATIC ELECTROCHEMICAL ANALYSIS: PART I

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I. INTRODUCTION

Increasing social interest in the results of analytical chemistry necessitated the development of automated measuring techniques. The increasing demand means, in economically highly developed countries, that 10 to 30 analyses are requested yearly per capita.

The use of the expression "automation" is common in the literature of chemical analysis, and it is most often not in consequence with the well-known IUPAC definition.

Most often any mechanization or any substitution of human effort is called automation. This wider, commonly understood meaning of the word is used in this work intending to show one side of the progress achieved in electroanalytical chemistry.

Imposing the general system concept, each automatic analyzer in itself is regarded as a system in which signals holding analytical information are generated, treated, filtered, and then converted to chemical information by an appropriate basis.

According to Malissa, the chemical information for the generation of a signal is based on the following reaction:

$$M + R = I$$

where M is the material to be examined — it means the smaller or larger part of the sample exposed to the reagent; R is any kind of reagent — chemical, photon, or electric energy; and I is the signal obtained.

Reaction of sample elements with the reagent usually yields a complex signal implying, on the one hand, a signal component originating from the reaction of the single element and the reagent or, on the other hand, the signal components produced by the reaction going on between the reagent and the other sample elements (matrix effect). The stochastic signal components are similarly included in the complex signal. The reaction taking place between the reagent and sample elements is defined by predetermined response functions. In an automatic analyzer system, the reaction between the reagent and sample elements is taking place in the signal-producing unit.

Besides the reagent and sample element, interaction also depends on the experimental conditions. In potentiometry the indicator electrode is considered to be the reagent; in voltammetry the reagent is the electron.

The other main functional unit of an automatic analytical system is signal processing. The aim of signal processing is to bring the signal into a form which is easier to decode. To expound the analytical information from the signal may require the use of numerical methods (convolution, transformation, pike elimination, smoothing, etc.).

In order to gain chemical information from analytical information, the signal has to be decoded. Decoding can be done with the inverse function of signal producing. Previous learning processes enable the decoding to be done with the required reliability.

An analytical method consists of different independent processes. Even the different processes of this analytical chain, such as sample pretreatment, analysis, signal evaluation, etc., can consist of different steps.

The trend is obviously to mechanize and automate each step. In different stages of development, however, mechanization or automation of a different level can be most effectively and economically used. Automation has two main goals in chemical analysis: the substitution of human labor and the ensurance of better analytical parameters. The latter can be the result of uniform sample handling, objective evaluation, and/or higher efficiency of the automatic method. Automatic equipment can ensure flexibility in solving a certain analytical problem, free of human interference and the source of subjective error.

In the following, we will survey the most important results achieved to date in the automation of electro-analytical methods. It should be noted, however, that the rapid development in microelectronics and the ever-increasing application of its results in the field of chemistry and analytical chemistry accelerated the development of measuring instruments to such an extent that it would be a very difficult task to give a full survey on the present state of progress. At the time of publication of this work, reports can surely be read about experiments carried out in order to develop a new generation of instruments, and some of the home-constructed novel types of apparatuses mentioned in this work as should-be-realized instruments will become commercial.

On this work — perhaps a little arbitrarily — the present situation of electroanalysis concerning its automation will be discussed in four separate groups (automation in potentiometry, automation in voltammetry, automation in titrimetric analysis, and analysis in flow-through channel). In the frame of each topic we will try to present the results in their progress. We do not plan to analyze in detail the general problems concerning the automation of quantitative chemical analysis and their possible solutions. Consequently, problems and instruments of the automation of sample preparation, theoretical questions of signal formation, and data processing will not be emphasized.

After referring to automation in preparing the samples, problems in the automation of potentiometric measurements in discrete samples will be discussed. Afterwards, results in the individual steps of automation of voltammetric analyses will be treated.

The group of titrators achieved quite a high level of mechanization or automation early in the history of instrumental analysis. A separate article in a later issue will be devoted to the introduction of a few members of the newer generations in this group.

Analytical devices applying a flow-through analysis channel, which have played an important role in the last 2 decades, will also be treated separately. It should be noted that mainly laboratory analyzers will be discussed in this work.

II. A FEW RESULTS IN THE AUTOMATION OF SAMPLE PREPARATION

Electrochemical analysis, in the majority of cases, is a wet chemical procedure. Thus, for discussing the preparation steps of mechanized, automated analyses, a short treatment of procedures and devices used in wet chemical analysis is necessary. In laboratory analyzers the sampling can be considered as the first step. Naturally, the mechanization, automation of sampling of solids, liquids, or gases means totally different tasks. A comprehensive survey of different types of mechanisms suitable for sampling solid, liquid, or gas-phase materials would be too far-fetched.

Most methods are for measuring liquid samples. Volumetric sampling units applied most frequently are the following:[1-4]

- Pipettes
- Reservoir provided with a liquid level controller
- Sampling plunger provided with suction and discharge valves
- Sampling rotating valve device
- Gate valve sampler
- Gate valve or rotating valve sampling unit provided with a loop
- Membrane chamber sampling unit
- Drop charger sampler
- Swinging balance volumetric unit

The individual types are known in many different constructions (size, structural material, etc.). Several of them are shown in Figure 1.

In analyzers applying the flow-through analysis channel principle, in addition to the above devices, peristaltic pumps are also frequently used. For mixing two liquids in a precise volume ratio that flow in the analysis channel, volume quantitation equipment with a bubble detector can be applied.[6]

The automatic sampling and preparation of solid samples for wet analysis represents a more difficult problem. The summarizing work of Kuzel et al.[7] contains applications of solid samplers; they are mostly used in the control of pharmaceutical preparations. The sampler of Gál et al.[8] realizes uniform pulverized material feed.

An important step in sample preparation is dissolving the sample, i.e., getting it into a suitable form for analysis. For this purpose, mechanized or automated crushing and grinding devices[9] and units applicable for destruction and digestion have been developed.[10-12] There are also technical solutions known for the absorption of gas samples.[13]

Automatic instruments suitable for carrying out separation processes eventually needed in analysis also have been developed for the application of mechanized and automated analyzers. Thus separation procedures such as dialysis,[14-16] distillation,[17-19]

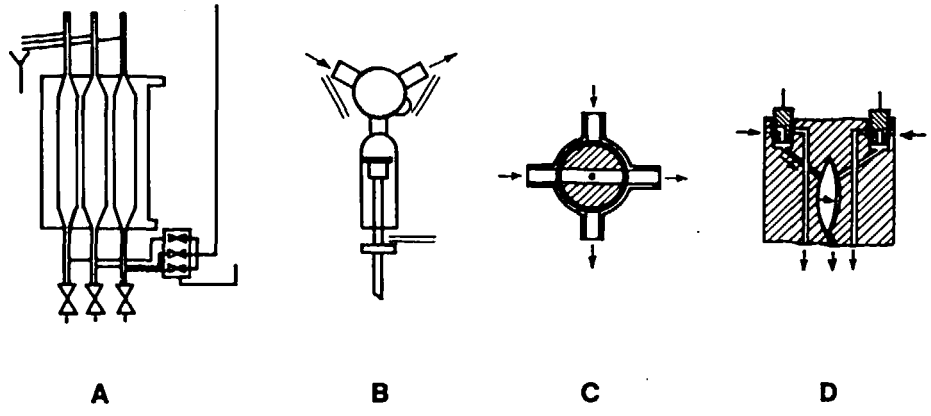

FIGURE 1. Volumetric sampling units. (A) Magnetic valve-controlled, three-headed pipette according to Pungor et al.[5] (B) Sampling unit with gate valve: (a) burette cylinder with plunger, (b) valve, (c) input of the sample, (d) output to the titration vessel, (e) rotation angle controlling cam, (f) microswitches for the servo-system of the valve, (g) plunger bar, (h) microswitch for inactivation of the plunger drive. (C) Two-way rotating valve: (a) volumetric valve channel, (b) sample inlet, (d to e) washing solution inlet-outlet. (D) Membrane chamber sampling unit: (a) membrane chamber, (b) membrane, (c, d) mechanized valves, (g) sample inlet (under pressure), (h) sample outlet, (i) washing solution outlet.

extraction,[20-23] and filtration,[1,2] as well as chromatographic separations[24] can be performed.

The solution obtained by the methods mentioned above frequently has to be subjected to a preparative chemical reaction preceding the actual analysis step, e.g., masking, preincubation, quenching, oxidation or reductive transformations, etc. For these reactions, appropriate reproducible administration of the reagent and adjustable reproducible reaction time and temperature have to be ensured. In several cases, extra care has to be taken in the mechanized, automated realization of this step of analysis.

The sample preparation steps mentioned earlier differ from each other to such an extent that their automation and mechanization pays off only for large series of samples in the case of highly automated devices for a certain purpose. On the contrary, the so-called wet chemical treatments are more uniform, thus their mechanization and automation for different analytical tasks do not require very different apparatuses. Therefore, the wet chemistry generally is done automatically in the commercial analyzers.

The sample preparation steps (similar to those of actual analysis) can occur on samples separated in space (batch analyzers) or separated in time, such as in samples in a flow-through analysis channel (flow-through analyzers).

The mechanization and automation of preparation procedures in batch-type systems requires mechanically more complicated instruments. It generally contains more moving parts susceptible to breaking down (valves, plunger, motor) and thus its maintenance is more difficult. Its control requires a more complex process. The advantage is, however, higher flexibility and easier reprogramming.

In flow-through analyzers, the preparation step can occur in the flow-through analysis channel itself. For the operation of the instrument only a few mechanical devices (a single peristaltic pump) are needed.

III. AUTOMATION IN DIRECT POTENTIOMETRY

The first step in the "automation" of potentiometric measurement was carried out almost 50 years ago, when the first electronic voltmeters appeared. The substitution of the compensating bridges with electronic instruments of direct analogue display considerably decreased the time consumption of the potentiometric measuring step of the analysis. In addition, an electronic voltmeter, due to its high input resistance, decreases the error caused by the polarizing current flowing in the circuit when the bridge is off balance.

A. Automated pH and pX Meters

The electronic voltmeter of high input resistance, equipped with a specific scale and amplifier offset and with temperature slope adjustment, permits automatic measurement of the pH of solutions upon accurate previous adjustments based on the measurement of emf values in standard solutions. Accordingly, the most widely used analytical instrument, the pH meter, can be considered as a kind of automatic apparatus. An increasing number of so-called pX meters appeared on the market as the use of different ion-selective electrodes gained importance. The pX meters permit the direct display of the negative logarithm of the activity of the ion in question on the basis of a potentiometric measurement. The pX meters must be equipped with a slope factor adjustment function of a wide range, since the slope of the calibration curve of ion-selective electrodes can differ to a large extent, depending on the charge of the ion and the characteristics of the ion-selective electrode. Irrespective of the occasional differences in electronic circuitry, the analogue pH and pX meters mainly differ in the pointer scale and in the extended range of the slope adjustment of the latter.

The next step of development was the appearance and spread of instruments giving a digital output signal ready for the digital data collecting units. Today, almost all firms manufacturing pH meters have their own selection of instruments with digital display and with output of some kind of coded digital signal. A pH meter-multiplexer combined unit is often incorporated in complex measuring systems employing potentiometric detection. Such units indicate a digital measuring signal drawn from several measuring cells according to a preset sequence or a special time program.

Determination of the proper time to take the cell potential readings is an important question in the practice of potentiometric measurement. A steady potential reading is observed in a certain — shorter or longer — time after bringing into contact the measuring electrode and the sample solution. However, a considerable drift of the electrode potential can occur if the waiting time is too long. This drift can be caused by various processes. The composition of the sample solution may be slowly changed as a result of sample-electrode contact. Changes in the salt bridge or in the reference electrode may also take place.

The development of instruments which automatically select the proper time for taking the readings is a trend in the automation of potentiometric measuring techniques. In this way, a considerable source of error is avoided. The principle of this selection differs in the case of various apparatuses. According to one method, the reading is taken or is displayed at a fixed time after immersing the electrode in the sample solution. The drawback of this method is obvious. The response time of an ion selective electrode is subject to change by aging. It is more advantageous if the time dependence of the electrode response is followed with appropriate electronic circuitry and the time constant for the reading is selected accordingly. In certain instruments, the reading may be taken just after the rate of change of the electrode potential has fallen below some

predetermined level. The rate of change can be compared either by observing the potential change during a fixed time, or the time required to attain a given change is followed. The $1/t$ vs. $10^{E/S}$ plot (if it is linear) can be used to predict the electrode potential at infinite time. The extrapolation of the straight line will intersect the $10^{E/S}$ ordinate at $t = \infty$, which corresponds to the steady-state reading. However, the $1/t$ vs. $10^{E/S}$ plot was not found to be completely linear in accordance with theoretical expectations. The Radelkis Company developed a remarkable automatic way of selecting the time of reading. The $\Delta E/\Delta t$ value is followed in time and the electrode potential (E) belonging to the smallest $\Delta E/\Delta t$ ratio is displayed as the reading by the instrument. This electronic circuit is relatively simple and inexpensive.

The Orion type 811 pH meter is a good example of the modern laboratory potentiometric apparatus. The instrument displays the cell voltage only after it has achieved a quasi steady-state value. Its temperature sensor automatically corrects the error caused by the temperature difference between the calibrating standards and the sample solution. When the potential difference observed in the measurement of two different standards deviates considerably from the theoretical value, this error is indicated.

Various integrated microelectronic units (microprocessors) have recently become less expensive and consequently could also be incorporated in small laboratory equipment. Thus, potentiometric instruments with a microcalculator and microprocessor having an increasingly sophisticated calculating or control function have appeared on the market. The extra services and the simple handling of these instruments, as well as the decrease of their cost, increase their popularity.

The Corning Ion-Meter 135® contains a built-in laboratory calculator which can also be used separately. The instrument permits the automatic use of six different measuring programs such as standard addition, sample addition, pH determination, etc. Various data can be stored in the memory of the calculator and used for the calculations.

The Beckman Select-Ion-5000® microprocessor-controlled pX meter carries out seven different measuring functions, in each case displaying the appropriate commands and performing the analysis through the required steps of the analytical procedure. Fifteen different routine analytical problems can be completely solved with all the calculations required.

The microprocessor-controlled pH Meter of the Knick® company (type 740) is another example of highly automated laboratory instruments for pH measurements. The Orion Ion-Analyzer 901® considerably simplifies the measuring procedures, performs a certain blank correction, and calculates the sample concentration by a built-in microprocessor. The blank correction is intended to decrease the errors caused by the slow electrode function and to linearize the E vs. log, a function in very dilute solutions when the concentration is near the lower detection limit of the electrode. The correction can be performed by adding a given amount of the component to be determined both to the sample and to the standard solutions. In this way, the rate of the response of the electrode can be increased and the linear range of the electrode function can be used for the determination. The increase of the concentration is automatically taken into account and, thus, accurate results can be obtained rapidly.

Three different operating modes — concentration measurement by calibration, known addition, and analyte addition — can be accomplished with the system. The functional block diagram of the instrument is shown in Figure 2.

B. Automated Analyzers Based on Potentiometry

In addition to the widely applicable and automated fundamental instruments, various more complex types of potentiometric measuring apparatus also have been developed as a result of the introduction of automation in potentiometry.

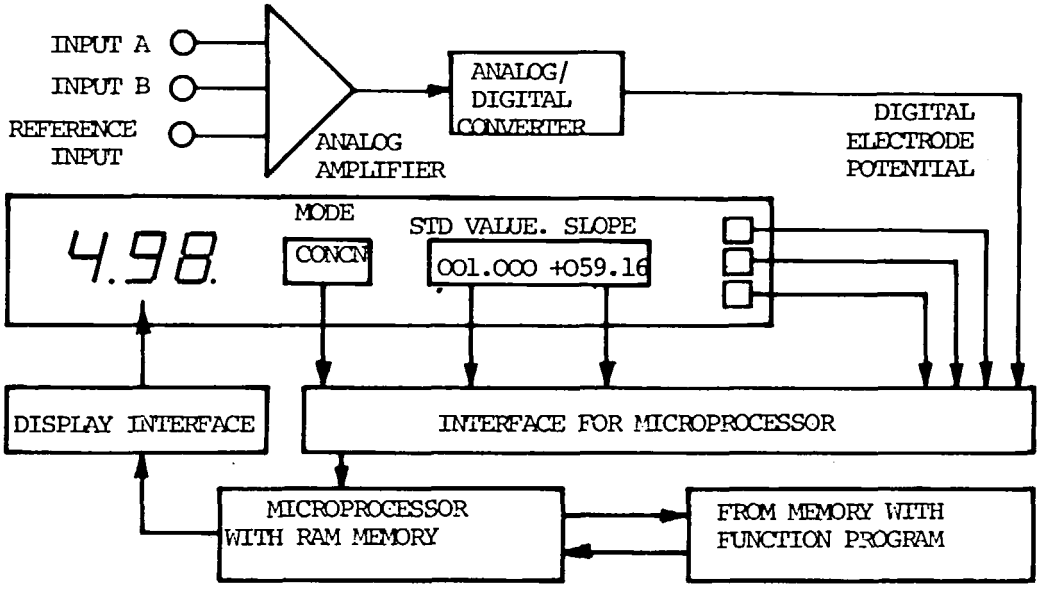

FIGURE 2. Block diagram of the Orion Ion-Analyzer 901.®

These instruments can be divided in two groups. On the one hand, single-purpose automatic potentiometric instruments were designed, permitting an efficient solution of important analytical tasks. On the other hand, a number of reports have appeared in literature about complex systems which can automatically perform one or more potentiometric methods or evaluation procedures. The above-mentioned papers most often described works in experimental or sometimes even in preliminary stages. The instruments in question will be introduced into industrial production and put into widespread use only if real needs can be satisfied economically. Some complex automatic instruments showing more or less advanced stages of automation of potentiometry will be mentioned.

The Radelkis OP-266 Biological Alkali Analyzer® can be considered an automatic single-purpose instrument: the sodium and potassium ion concentration of whole blood is determined with ion-selective electrodes. As a matter of fact, marketing of apparatus used for the determination of potassium and sodium content in clinical samples is very attractive for a company manufacturing electroanalytical instrumentation. The reason for this is that in many places the users of the old flame photometers seem to be in favor of changing from a flame method to a highly automated potentiometric one also being safe to operate.

Accordingly, quite a few apparatuses were developed, e.g., the NOVA 1® equipment of NOVA Biomedical Laboratories, Model SS-30® of ORION, and the ASTRA® of Beckman. All of them use valynomycin-based potassium and glass-based sodium sensors. The operation and evaluation is accomplished by computer or microprocessor. Quite a few firms, e.g., the ORION and the NOVA Biomedical Laboratories, manufacture automatic apparatus for the determination of ionized calcium content of blood. This problem appears frequently in the practice of clinical laboratories. Both the type SS-22® apparatus of ORION and the NOVA 2® of NOVA Biomedical Laboratories use a peristaltic pump for the introduction of the sample, previously treated with appropriate reagents, into the flow-through measuring cell containing an ion-selective electrode. All operation of

the analysis, including the rinsing of the apparatus and the calibration between measurements, is controlled by an electronic control panel in the SS-22, while a microcomputer controls all the above in the NOVA 2 instrument. The ORION apparatus is a bit older in design and its operation requires a little more operator assistance (injection of samples, reading and taking the results one after the other). The Acid-Base Meter®, type OP-213, (produced by Radelkis) after proper calibration automatically displays the concentration of various acids and bases. Its measuring function is based on a new concept, the so-called linear response reagent mixture principle, which will be described briefly later, and direct potentiometric measurements are performed with hydrogen ion-selective electrodes.[25]

The importance of an apparatus capable of the determination of blood-gas or blood acid-base balance is obvious in clinical analysis. Accordingly, these have achieved widespread application in different clinical laboratories. Different types of blood gas analyzers are made to determine a few important parameters of human blood. They contain a potentiometric measuring cell, and thus it is reasonable to mention them here. The ABL-2 Acid-Base Laboratory® of Radiometer is a remarkable unit among the different automated blood-gas balance measuring instruments. The function of the apparatus is controlled by a microcomputer. It performs three different jobs: the calibration using two standards for each measured parameter, the analysis, and the rinsing of the cells. One measurement requires a 200-$\mu\ell$ blood sample. Besides the potentiometric pH and carbon dioxide electrodes, other sensors are used: an electronic barometer, a Clark-type amperometric oxygen sensor, and a photometer for the measurement of blood hemoglobin content. After the automatic evaluation of the measurements, the apparatus calculates six further parameters of diagnostic importance from the five measured ones using appropriate equations, and it prints out all the measured and calculated parameters.

An automatic apparatus has been worked out by Tomcsányi[26] for the determination of fluoride content of gas samples; it can be used in the control of pollution. The apparatus — which was named Fluchek — works on the zero potentiometric principle; it follows the cell voltage between two half cells, each containing an ion-selective fluoride electrode. One of the half cells is filled with a standard fluoride solution of a certain concentration while a buffer solution with no fluoride is in the other. The air or gas sample bubbles through the absorbing buffer solution with a constant, known flow rate. The calculation of the fluoride content of the sample is automatically done from the time required to achieve a zero voltage difference. At a constant flow rate, this time is inversely proportional to the fluoride concentration. The apparatus digitally displays the fluoride concentration in concentration units.

C. Noncommercial Automated Potentiometric Systems

Reading the scientific literature on potentiometric techniques, one can easily come to the conclusion that Sekerka and Lechner[27-30] made an important contribution. They developed an automatic measuring apparatus for potentiometric determinations. Several reports have appeared about further improvements of the apparatus.

The version[27] used for the determination of low concentration of fluoride ion was assembled from an Orion® model 601 ion-selective fluoride electrode as the detector, Orion type 751 digital printer, Orion® type 801 digital mV/pH meter, and a De Saga peristaltic pump. A Fisher® type 9-319-50 thermostating electrode elevator turntable unit and a homemade control module completed the apparatus. The block diagram of the apparatus is shown in Figure 3.

The following functions are performed by the apparatus: TISAB solution is added to the samples placed in the sample holder, the sample is mixed, and the electrode system is immersed in the sample container serving as the measuring cell. At an adjustable fixed

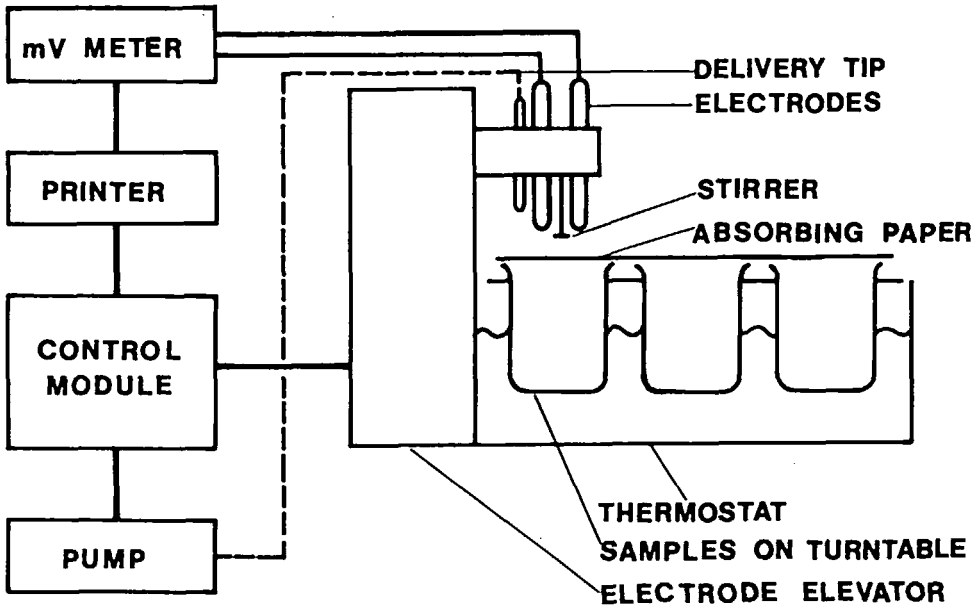

FIGURE 3. Block diagram of the automatic potentiometric measuring apparatus used by Sekerka and Lechner.[27]

time after these functions, the cell voltage is measured and printed out. This is followed by the intensive washing of the electrodes and the next sample analysis is started.

The control module has a process control function and permits flexible measuring programming to be devised. However, a relatively long analysis time, e.g., 10 min, had to be chosen in order to attain an acceptable precision in the case of samples less concentrated than 10^{-6} mol/dm^3 because of the lack of a feedback connection between the detector and the control module. Another drawback is that the stabilization of the cell voltage is not checked. The next version of the apparatus[28-30] incorporated a Wang 600 minicomputer and a printer connected through an appropriate interface (Figure 4). It permits conductivity and pH measurements to be carried out in addition to direct potentiometric analysis. The potentiometric water hardness determination — which is the main purpose of the apparatus — is made with the standard addition method combined with a subsequent dilution (1 + 1) and electrode potential measurement. (A practice we prefer is to use the symbology of (X + Y). When (X:Y) is used, some people read it as X parts of the first substance diluted with Y parts of the second, while others may read it as X parts diluted to a total of Y parts. The use of the plus sign instead obviates the difficulty.)

The carbonate hardness (C) is calculated by the computer on the basis of:

$$C = C_s \left[\text{antilog} \frac{E_o - E_1}{29.5} \right] \qquad (1)$$

where C_s is the $CaCO_3$ concentration in the standard (ppm), E_o is the electrode potential measured in the standard solution (mV), and E_1 is the electrode potential measured in the sample (mV).

The total hardness (C_T) is calculated according to the following equation:

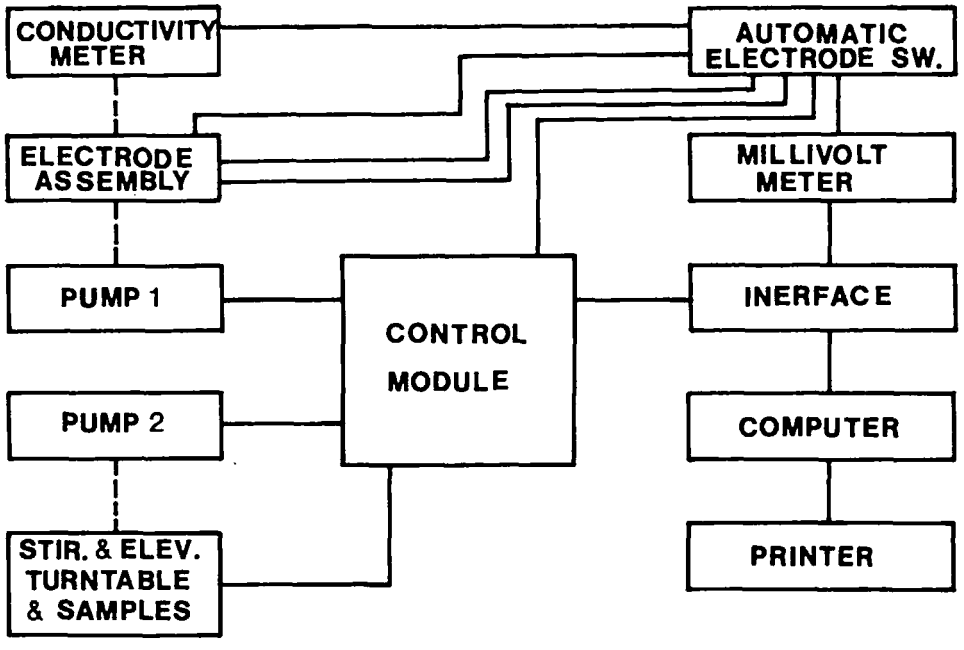

FIGURE 4. Block diagram of the instrument used by Sekerka et al.[30]

$$C_T = C_A \left[\text{antilog} \left(\frac{\Delta E \log 2}{E_2 - E_3} \right) - 1 \right]^{-1} \qquad (2)$$

where C_A is the $CaCO_3$ concentration of the standard used for the addition (ppm), E_2 is the electrode potential measured after the standard addition, and E_3 is the electrode potential measured after the dilution to a 1 + 1 ratio.

$$\Delta E = E_2 - E_1$$

The measuring process is still controlled by a separate control module in spite of the application of a minicomputer. There is no feedback connection between the measured results and the control unit. The apparatus permits the analysis of 20 samples in 1 hr. The flow chart of the program is shown in Figure 5. The electrode potential data is measured at a fixed time after the immersion, or standard addition or dilution, respectively.

The co-workers of the Netherlands Energy Research Foundation[31,32] reported the application of a computerized automatic system — developed earlier for wet chemical analysis — for potentiometric ion-selective electrode measurements. The system is based on a PDP-11-03 LSI processor having a 24-K core memory capacity. The appropriate central interface permits high-level control of the functions of all units (sample handling, dilution burette, data display, etc.). The block diagram of the system is shown in Figure 6. The mechanical movements needed for sample handling are propelled with pneumatic cylinders and the piston of the precision burette is driven by a stepping motor. The sample transfer system and the diluter are shown in Figure 7. The programs elaborated for the apparatus contain a built-in command system with multiple checking functions required for safe operation. If necessary, an error signal is displayed and the analysis is repeated. The programs for the evaluation of the signals follow simple conventional methods despite the high number of other possibilities offered by the computer.

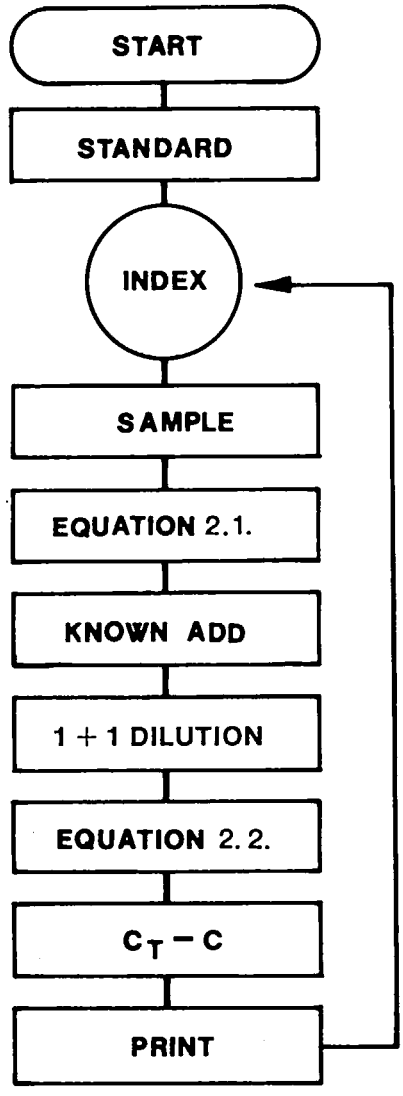

FIGURE 5. Flow chart of the computer program used for the standard addition measurement by Sekerka et al.[28]

The apparatus permits the calibration of the electrodes according to the programs. The calibration is repeated (not more than four times) if the repetition of the calibration results gives significantly different electrode potential data. The calibration is checked with a standard solution at certain time intervals during the measurements.

Another measuring program permits the analysis with 20 precalculated standard addition steps. Blank correction is employed by calculating (with curve fitting) the concentration correction in advance. This operation offers a specific advantage in the analysis of a diluted solution. The measuring system gave reliable results in the analysis of the concentration of various ions in rainwater. The precision of the results exceeded that of manual methods. With standard addition and the direct potentiometric method, 15 and 25 analyses, respectively, could be performed in 1 hr. In our opinion, a similar

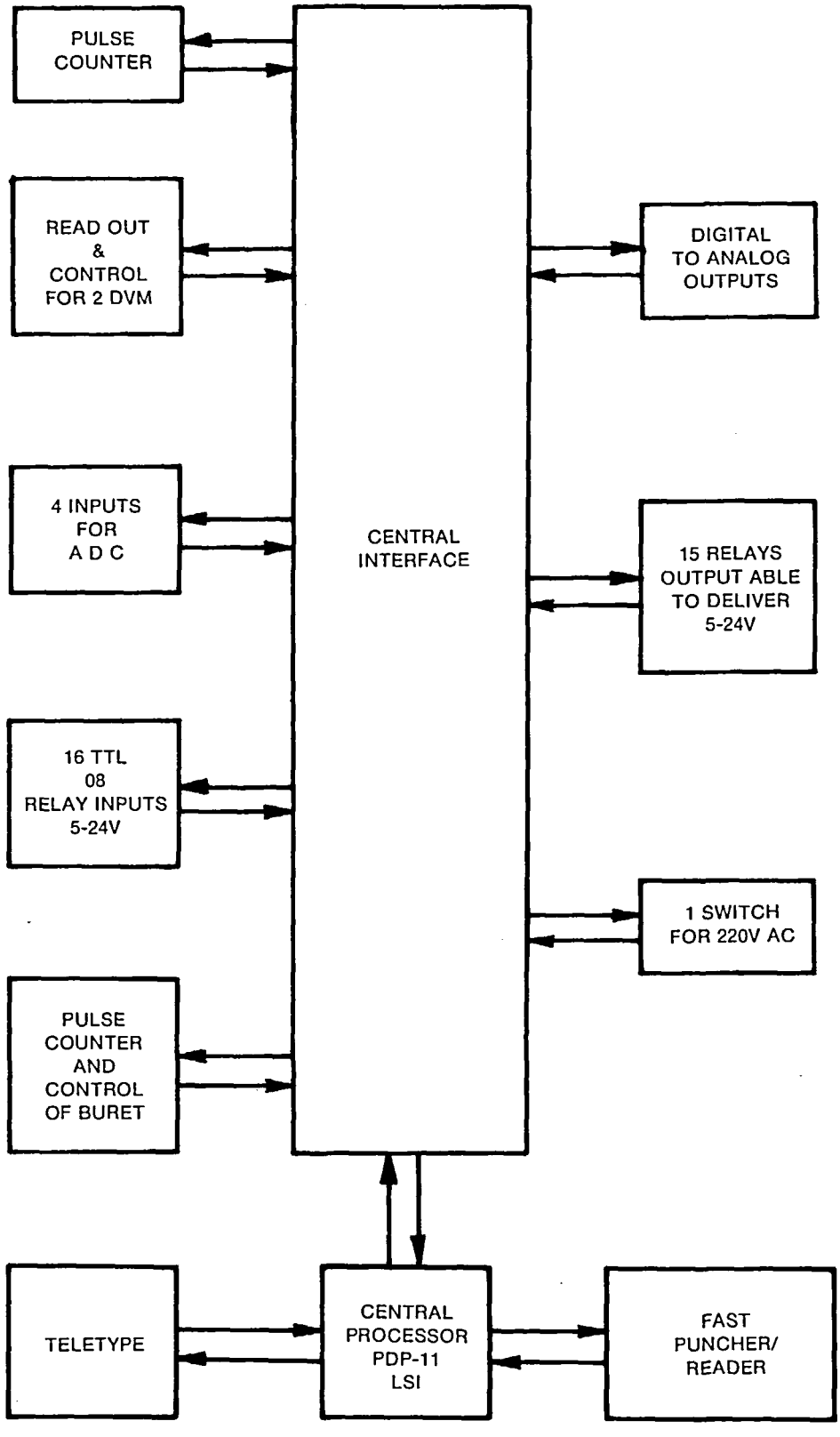

FIGURE 6. Computer system employed by Slanina et al.[31]

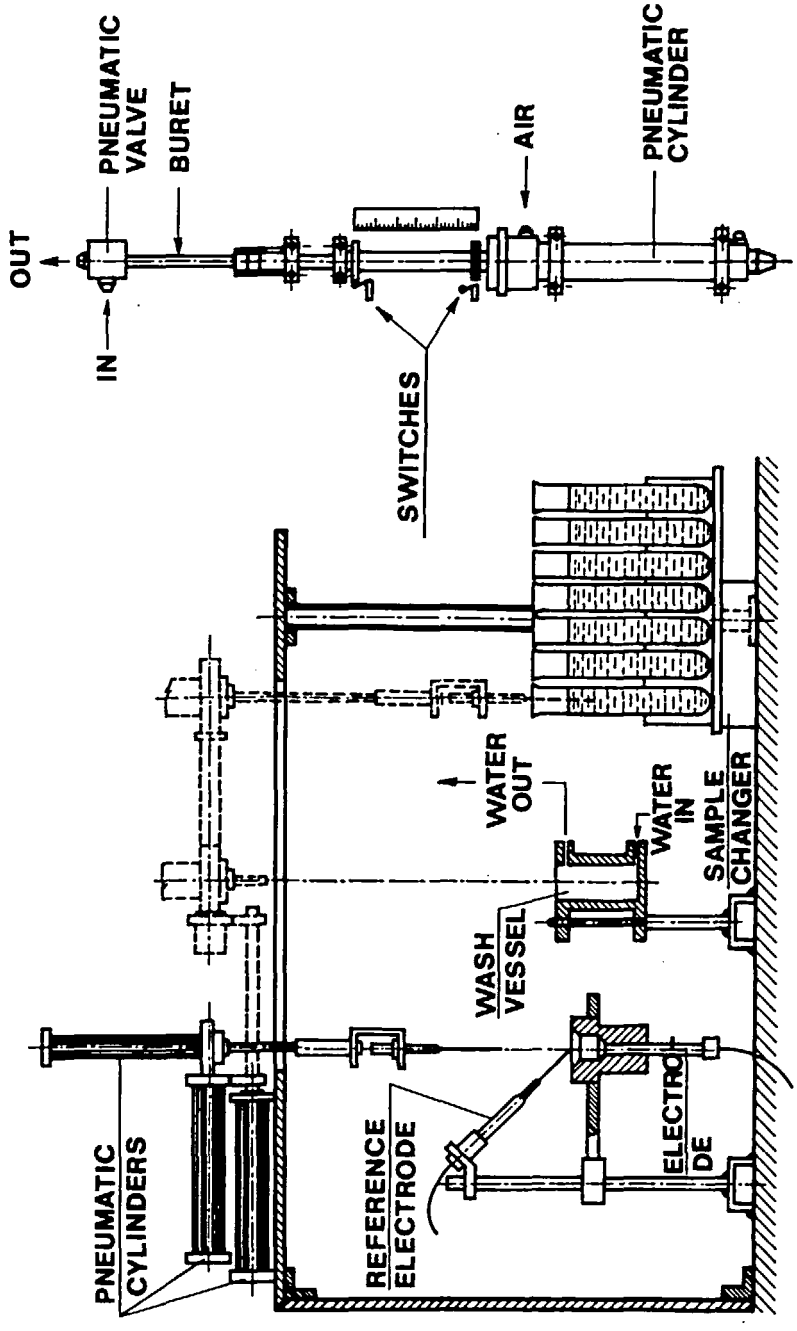

FIGURE 7. Sample transfer and diluter system employed by Slanina et al.[31]

performance may also be obtained with simpler and less expensive potentiometric equipment.

In 1976, Ariano and Gutknecht[33] published an article on the development of a computer-controlled potentiometric analyzer with a much simpler mechanism. The function of the apparatus is based on the multi-standard addition measuring method. The voltage of the potentiometric measuring cell consisting of a cation-selective glass electrode and a saturated calomel reference electrode is digitalized with an AD converter and fed into the computer, which collects the data after adequate noise filtering. The computer follows the cell voltage vs. time and selects only stabilized readings. A solution-carrying system which ensures a constant flow rate serves for the addition of various volumes of the standard solution. The computer controls the volume of the standard solution added by determining the time period during which the addition valve is kept open. The switching of the stirrer at the correct time is also automatic.

The time period of the analysis is mainly determined by the time period needed to collect the number of cell voltage and volume addition data pairs fixed in the program. Since the response curve is actively followed, the response time of the electrode determines the actual time of taking one data pair. No overlong waiting time is needed.

Selection of the volumes of the standard portions to be added successively is also the function of the computer. According to the program, the computer determines the standard solution volumes, the successive addition of which produces nearly equal changes of the cell voltage. The unknown concentration is calculated by fitting the volume and cell voltage data pairs to the Nernst equation employing a nonlinear least-square fitting method. The apparatus was proved to be applicable for the automatic determination of potassium ion above 10^{-4} mol/dm.[3] With some improvements in the mechanical part of this apparatus, a useful automatic analyzer could have been worked out.

The Gran linearization can be advantageously used for the evaluation of titration curves and standard addition or subtraction measurements. A small computer connected to the measuring instrument can be very useful in calculating the Gran-transformed function of the data, especially in the case of a large number of data pairs. It is often observed that certain sections of the Gran function do not fit on the theoretically expected straight line. Different factors can be responsible for this phenomenon. This curvature hinders the application of the Gran relationship in automatic potentiometric analysis.

Frazer and co-workers[34,35] discussed the application of the Gran transformation in the evaluation of titration or standard addition curves and developed a method applicable for automatic evaluation. The so-called error function left (EFL) method permits the selection of the linear section of the Gran function in which the behavior of the measuring cell best approaches the theoretical one. The method consists of first selecting the apparently linear section of the function in which the linearity test is intended to be done. An appropriate window size is selected, then the window is stepped in the apparent linear range with an adequate step size ensuring sufficient overlapping of the data fields. A line is fitted on each data field with linear regression. Each line intersects the reagent or standard volume axis. The relationship (EFL) which is used to simplify the evaluation is obtained by plotting the differences of the consecutive values of intersection volume as a function of the reagent added. The minimum of this plot corresponds to the linear theoretical part of Gran transformation in the case of properly selected steps and window size.

The applicability of the method was shown by several examples. The dependence of the shape of the auxiliary plot on different parameters has also been discussed. The method appears to permit the reliable and precise evaluation of the results obtained with

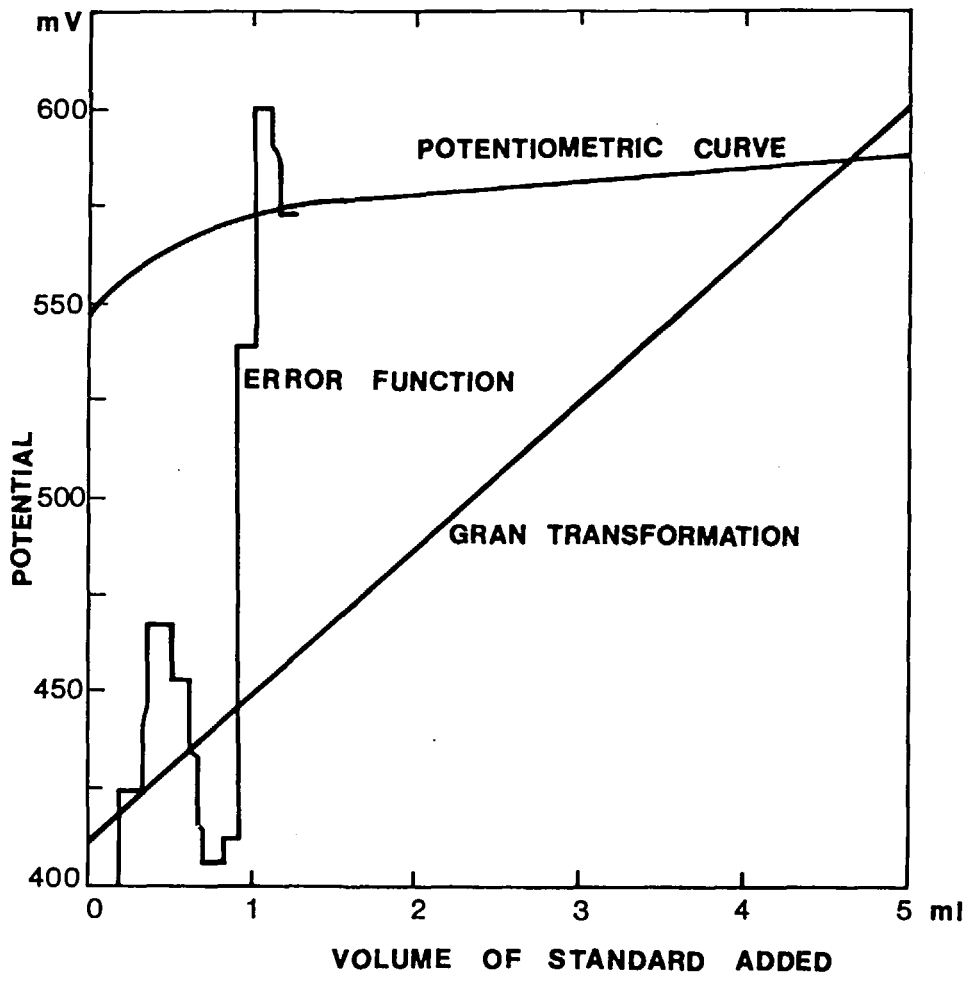

FIGURE 8. Potentiometric curve, gran transformation and error function plots, respectively, for the determination of 10 ppb of active chlorine obtained by Frazer et al.[36]

automatic potentiometric measuring systems. However, the time-consuming transformations hinder the application of the method, unless an on-line computer connection is available, since 511 cell voltage-reagent volume data pairs with 30 data windows and 15 data step sizes have been proved to be necessary in order to attain an acceptable precision in the definition of the end point of a titration curve.

Frazer and co-workers[36] published another paper on the application of the method. A measuring system was designed for the determination of dissolved chlorine gas in water. An Orion type 97-70 residual chlorine electrode was used as the sensor. The system consisted of the following parts: Mettler® DV 11 digital burette, PDP 8/1 computer, and GT-44 and PDP 11/45 units. The computer units automatically control the multistandard additions, the potentiometric measurements, and the evaluation. The latter is carried out using the Gran relationship and the error function auxiliary curve. The curves used for the evaluation of the results are shown in Figure 8. The concentration to be determined is obtained by the extrapolation of the line fitted to the data field of the section of the Gran-transformed curve corresponding to the error function minimum.

A more advanced version[37] of the above system was also employed to determine

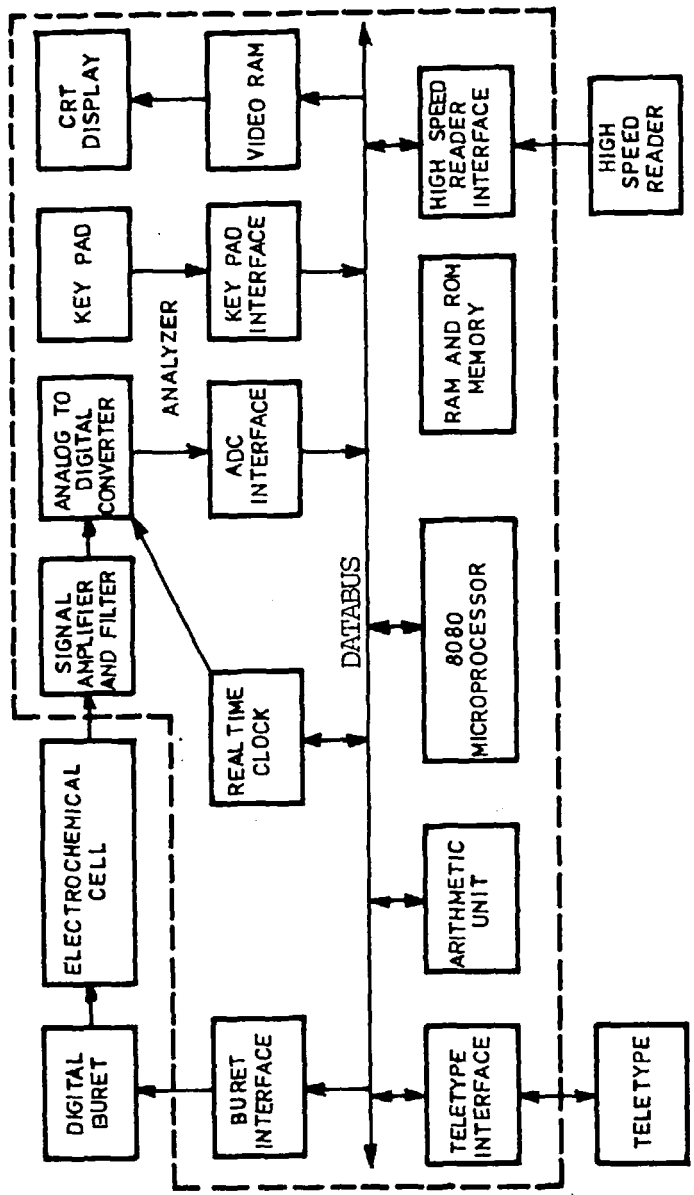

FIGURE 9. Block diagram of automatic analyzer used by Frazer et al.[37] for chlorine determination.

dissolved chlorine in water with the potentiometric standard addition technique. In this case, the standards were added at short intervals and the cell voltage readings were taken one second after the addition. The cell voltage readings obtained in this way were evaluated as described before. It was found that 126 data pairs ensured excellent reproducibility (relative standard deviation $\leqslant$1.14%).

Earlier, Frazer and co-workers designed an automatic analyzer for potentiometric measurements (Figure 9). The analyzer operated in both titrimetric and multistandard addition mode. It consisted of a PDP-8/I computer, Mettler® DV 11 digital burette, an AD converter, a measuring cell containing ion selective electrodes, a plotter, a teletype, and other units. The complete operation of the system is controlled by the computer. Thus the latter controls the steps of the analysis, the frequency of the reagent or the standard addition, its increments, the data collecting, and determines the start and the end of the measurement.

After the measurement, the computer automatically calculates the result from the collected data. The apparatus was used for the micro determination of phosphate in the presence of high fluoride concentration.[38] Lead perchlorate reagent and an ion-selective lead electrode were used. In order to determine the end point, the computer calculated the second derivative $\Delta^2E/\Delta V^2$ vs. V function and from one section of the latter containing 25 data points evaluated the end point volume with linear interpolation (V is the volume added). Selig[39] used the analyzer system similarly in the determination of sulfate in the presence of phosphate. An ion-selective lead indicator electrode also was used in this case and 0.005 mol/dm^3 barium perchlorate was employed as the reagent.

Selig and co-workers[40] developed a multistandard addition method for the determination of ammonia using the above-mentioned automatic potentiometric apparatus and an ammonia gas electrode. The evaluation of the results also followed the method mentioned before. The relative standard deviation of the results was less than $\pm$2% down to concentrations of 1.5×10^{-6} mol (20 ppb).

IV. AUTOMATION IN VOLTAMMETRY

For the relationship between automation and voltammetric methods, the following generalities can be made with respect to the earlier sections. Without exaggeration it probably can be stated that the effective utilization of voltammetric laboratory methods requires the application of automation to a higher degree than that of potentiometric methods. This is easy to see when considering the fact that the signal produced by a voltammetric measurement is, in fact, a function whose decoding (i.e., revealing its analytical information) is quite tiresome and frequently requires a lot of effort.

Accordingly, ever since the early application of voltammetry, significant efforts have been made towards automation. Early ones do not fit the definition of being automated. However, in the early stage, all the technical difficulties of the polarographic and voltammetric measuring techniques (duration, unsatisfactory sensitivity, problems of evaluation, troubles of handling and operating of electrodes) could not be overcome, and this made many analysts turn to various other methods, because at that stage the problems of automation either could not be solved at all, or only with difficulty. At the same time, researchers engaged in polarographic research focused their attention mostly on the theoretical problems of polarography.

Due to the general progress of automation and the possibility of applying new electronic and computational techniques, however, polarography and voltammetry have not only made up for lost time, but advanced considerably as was demonstrated by the Heyrovsky Memorial Congress held in Prague during August 1980. Here, in a whole

section of oral presentations, two plenary lectures and 19 of the poster presentations were dedicated to the new results achieved by automation.

The period beginning with the 1960s, the so-called renaissance of polarography, has brought about considerable progress in the field of automation. As a matter of fact, there is still a lot to do to change the image of polarography to a trouble-free, easily employed method, and automation can do the most for this.

In spite of the fact that the second generation of microprocessor-controlled automated polarographs has already appeared on the market, the use of proven, economically operated equipment for general use, utilizing digital electronics and computer techniques, is only in an initial stage.

Later, the results of automation of polarography and voltammetry will be discussed in the following sequence. First, the solutions simplifying the operation of the dropping mercury electrodes will be surveyed and then the results of efforts made for automating the two electronic units of basic polarographic equipment will be summarized. Some representatives of automated analysis systems using a voltammetric measuring technique will be discussed separately.

A. Improvements on Working Electrodes

Development of an analytical method based on microelectrolysis is possible only when the electrodes have strictly reproducible properties. This explains the fact that although the principal laws of electrolysis have been known since the last century, their analytical application was retarded until Heyrovsky's brilliant discovery: electrode of automatically renewing, reproducible surface. Considering this, it is possible to say that the development of the polarographic technique was feasible by a primitive form of automation.

A new field of chemical analysis was opened with the application of the dropping mercury electrode, simultaneously raising numerous problems solved only at a higher stage of automation.

From among these problems the most important is that of controlled drop time. To ensure a controlled drop time, a simple mechanism was used — the dropping electrode supplied with an electromagnetically driven hammer. This type of hammer-control drop time is a well-proven and generally used aid in classical d.c. polarography.

Drawbacks of this type of drop dislodging present themselves, first of all, in the case of highly sensitive analyses. The strong beat on the capillary, on the one hand, increases the capillary effect and, on the other hand, causes undesirable convection in the liquid contained by the cell system. As a result of these, the reproducibility of measurement results becomes unfavorable.

To eliminate these problems various automatic drop dislodging devices have been used. Undoubtedly, the electrode holder of the polarographic analyzer type 174A manufactured by PAR is worth mentioning. Here, drop dislodging is done with the help of a mechanized, crescent-shaped clamping slider securing the electrode. At the periodic interval selected by the clock switch, the clamp securing the capillary makes a short, quick movement, precisely detaching the mercury drop at the end of the capillary. Another solution is where the mercury flow is controlled by a solenoid valve. Tenygl and Fleet[41] developed a controlled drop time mercury electrode by streaming the mercury with a peristaltic pump.

An elegant drop cutoff technique was used by Hanekamp and Bos[42] applying an appropriately chosen potential pulse. When choosing the potential it is important to take into consideration that upon the effect of potential pulse, change in the capillary glass must not occur: on the other hand, if a relatively low potential pulse is employed, only a mercury drop of limited size is dislodged.

Fujiwara and co-workers[43] used a special drop syncronizer in their computerized polarograph. In this unit a piezoelectric barium titanate crystal was built in the capillary holder, which gave a mechanic shock when a pulse voltage of 200 V supplied by the computer-controlled timing system reached it.

In our opinion, the truly up-to-date mercury electrode is required to fulfill the functions of both the hanging mercury drop, as well as the classical dropping mercury electrode with the help of a controllable electromechanism. Electrode systems type 303 and 310, respectively, produced by PAR Co., can be regarded as its successful realization.

In flowing solutions the measuring cell can be shaped in such a way that after a certain drop growth the mercury drop is dislodged by the effect of the hydrodynamic pressure arising in the analysis channel.

The control of the drop time with appropriate automation not only provides the uniform drop size, but in this way the measuring program and the state of mercury drop can be synchronized.

Sturrock et al.[44] reported a stationary mercury drop electrode which has been developed from a syringe-type, hanging mercury drop electrode, operating it with a computer-controlled step motor.

For solid electrodes ensuring a reproducible electrode surface, automation — in a broad meaning — can be of help. The reproduction and protective conditioning of the electrode surface, the covering of the electrode surface with an electroactive film, and cleaning of the electrode surface can more or less be done automatically.

To perform long-lasting and continuous measurements, Novak[45] suggested a solution according to which the working electrode is polarized only for short time periods in given intervals, thus protecting the working electrode. Many different mechanical electrode surface-regenerating methods and techniques have been worked out. Some of them employ mechanized apparatus.[46,47] In industrial analysis, a proper cleaning brush is often placed into the measuring cell and rotating rubbing cleans the measuring surface.[46]

In the course of the measurements to ensure an electrode surface of the same property, frequently the sample and some conditioning or cleaning solution, (e.g., supporting electrolyte) alternately flow through the measuring cell — primarily in analyses of flowing solutions. The measuring process is controlled either by a simple mechanism or by automation.[47,48]

It is also widely known that polarization by a potential of opposite sign or direction, compared to that used to the analysis, often has a cleaning effect, too. These phenomena are utilized in the automation of cyclic voltammetry.[49,50]

There also are other methods whose principles are to use the necessary working polarization potential and a "cleaning" potential alternately.[51,52]

Tenygl[53] and also others[54] suggested an electrode (platinum) cleaning method in which a periodic electric heating of the electrode in a gas phase is done automatically.

B. Automation on Taking Polarograms

In polarographic voltammetric measurements, the unit which ensures the electrode potential-time program is of vital importance. The early manual potential divider circuit used only at the dropping electrode was soon replaced by a synchron- or step-motor driven potentiometer. The next improvement was to use the various program generators applying solid-state electronics, less susceptible to failure and ensuring high flexibility, which made superfluous the use of mechanical potentiometers that often became corroded under laboratory conditions. As a matter of fact, these program generators made possible the realization of modern measuring techniques favorable from different points of view. Due to these, examinations of voltammetric phenomena, as an effect of various potential-time functions (e.g., sine-wave, square-wave of different frequencies,

step), square impulse of increasing amplitude became possible. Furthermore, without electronic program generators, rapid polarization techniques could not, of course, have been developed at all.

The on-line digital computers having an appropriate configuration offer computerized control of the applied potential. This provides a high level of flexibility.

In voltammetry, the signal is a result of a current measurement resulting from applying an appropriate electrode potential-time program. Both are obtained by electronics of different complexity. The responses (currents) corresponding to results from the applied potentials have been measured by many devices, i.e., a mirror galvanometer through the frequency-selective amplifier of sine-wave polarography. A wide range of types of exciting signals of different properties that produce the current signal is known. Their detailed treatment is, however, beyond this work.

The current-electrode potential function serving as the basis of the voltammetric method being used is recorded in a more or less processed form. In the polarographic, voltammetric practice, the signal processing is usually done in an analogue form, with X-Y recorder, in the case of very fast techniques, with a cathode ray oscilloscope. This way of signal recording does not differ essentially from that suggested by Heyrovsky, the mirror galvanometric photoregistering equipment.

Introduction of digital data acquisition systems has enabled qualitative progress from the point of view of data acquisition and storage. Voltammetric data entered into storage systems of appropriate resolution and capacity can optionally be changed and transformed. Then the transformed voltammogram can again be displayed in analog form or processed further when required.

In the case of digital data storage, the main advantage is that the polarogram or selected sections of it can be appropriately displayed. This means reduction of time in searching for the appropriate sensitivity and potential range.

C. Data Handling

In polarography, automation gained widest application in processing the raw data. In this aspect, the special properties of the dropping mercury electrode necessitated making corrections for capacity and resistance of the electrode/solution interfaces; thus RC signal damping has been used very early in the application of polarography. When analog amplifiers were put into polarographs, the compensation was facilitated further.

The third primitive data processing technique is the application of analog derivation circuit by which the relationship $\frac{di}{dE}$ vs. E can continuously be produced. Now, however, automatic processing of voltammetric data acquired and stored in digital form can contribute enormously to the improvement of measuring the analytical parameters of the method. Among these possibilities, the following should be pointed out:

1. In the case of an analog instrument, it is of vital importance to choose the adequate sensitivity for recording the polarogram. Elaboration of an analytical method can disadvantageously be prolonged by experiments done for choosing the proper sensitivity with various polarograms. By digitalizing and storing polarograms this time can be reduced, namely, the stored polarogram or its sections can be displayed under various sensitivities.
2. The digital storage of polarograms permits different numerical corrections, thus helping the evaluation.

Utilization of results from automation has brought about significant development hitherto, although we are still in the stage of surveying the possibilities. Up until now, since few laboratory instruments could be conveniently connected directly to a

digitalized data collecting system, most initial attempts at automation used off-line data processing. At the same time, however, several research groups prepared polarographic set-ups using on-line connection with computers of different capacities.[55-57]

In the following section, results achieved by digital computation units that were developed by various research groups will be discussed and some examples given.

The new universal polarographs, able to store the polarograms in a digital form and to perform calculations and corrections on the polarographic data, induced the application of such polarographic techniques which earlier could not be widely spread because of experimental difficulties. For example, several advantages in the measuring technique are offered by placing two indicator electrodes of similar properties into two analysis cells and measuring the difference between the currents flowing through the two electrodes with an appropriate bridge circuit. To ensure two fully identical indicator electrodes is, undoubtedly, not a simple task. The up-to-date polarographic analyzers directly provide the above-mentioned advantages.

Most equipment, however, follows the classical method of polarography using a single indicator electrode. Thus, the standard operation scheme of the microprocessor-controlled polarograph PAR Model 374® includes, as a first step, the recording and storing of the polarogram of the background electrolyte and then the polarogram of the sample is corrected for the background value. The same electrode is used for measuring the data necessary for correction and those of the sample.

For the evaluation of overlapping polarographic waves and peaks, a very simple approach is described by Bond and Grabaric.[58] This method is based on the subtraction of polarograms relating to identical electrodes, i.e., electrode potential-current intensity data (overlapping polarographic peaks or waves) gained from the sample containing material A and B together, are stored in the memory of the polarograph. Afterwards, the concentration of the one component (A) is changed in a clean blank solution and a polarogram is recorded and subtracted from that of the sample until a peak, characteristic solely of the concentration of the other (B) material, is obtained. Obviously, if the concentration of material A is higher in the blank solution than in the sample, then negative values are the result, while at a lower concentration of material A, the different polarogram indicates two unresolved peaks. The flow diagram of the method and the simulated curves representing its principle are shown in Figures 10 and 11.

This method offers several advantages, e.g., it is very simple, no information is required about the electrode process and data for the calculations. At the same time, however, the experimental time needed to find the adequate concentration value may be very long.

Sample analyses giving overlapping voltammetric curves can, of course, also be performed in other ways with the help of greater computation apparatus. In this field, Perone and co-workers carried out large-scale investigations, partly with simulated voltammograms and partly with real curves.

Perone and Gutknecht[59,60] applied the numerical deconvolution technique for the analysis of solutions containing a 1000:1 mixture of components having 150 mV peak potential difference or components characterized by peak potentials close to each other (35- to 40-mV peak potential difference). The voltammograms have been described by empirical equations whose constants were different for different components. Using constants valid for the individual components and stored in the computer, standard polarograms were generated and their combination was fitted to the polarogram of the sample. The best fit gave the composition of the sample. Various Hewlett-Packard computers with the necessary accessories were connected to the measuring system. The methods elaborated have been tried out by the analysis of solutions containing Pb and Cd and Cd and In ions, respectively.

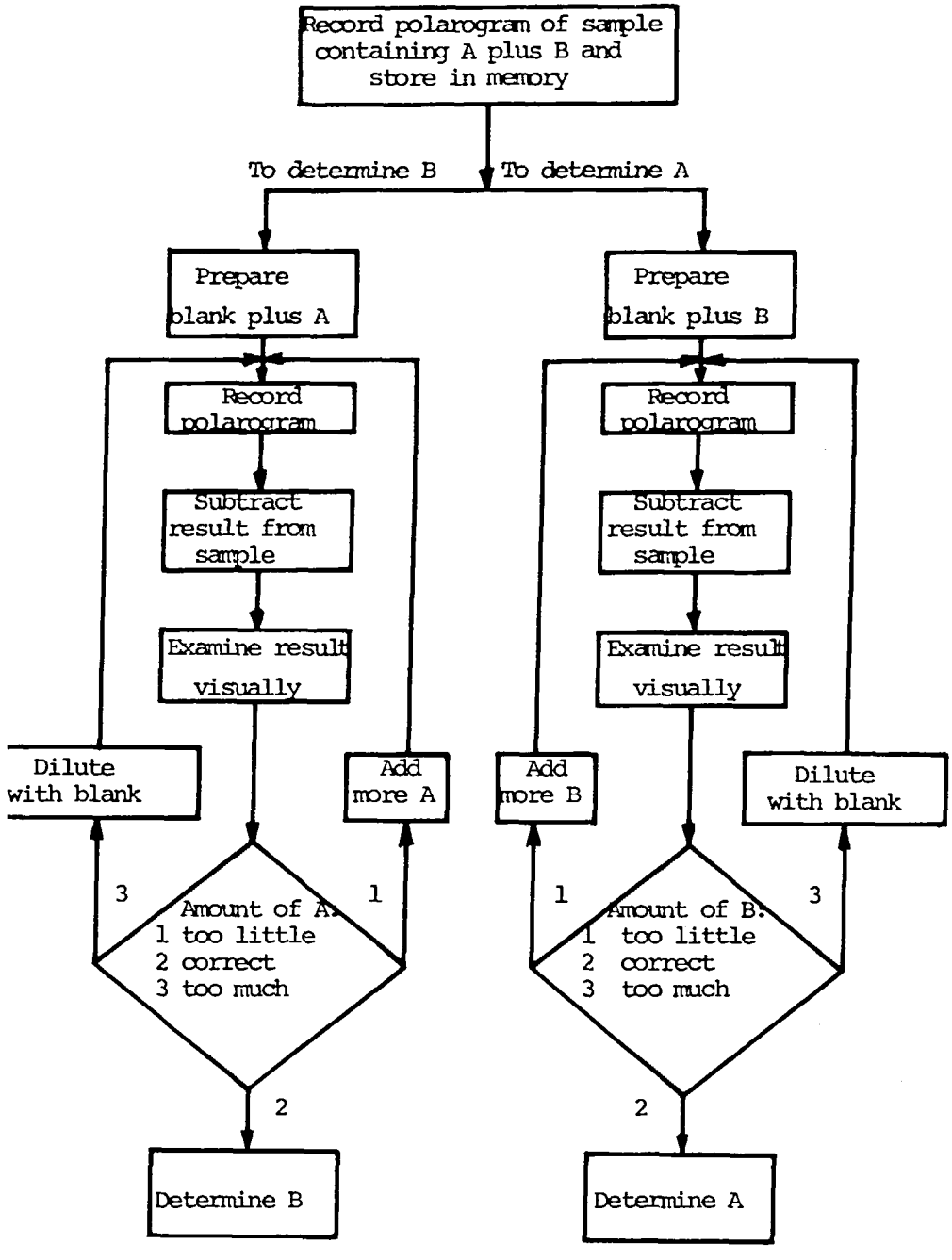

FIGURE 10. Flow diagram of the method for determining two species giving rise to overlapping waves, according to Bond and Grabaric.[58]

Perone and co-workers[61,62] also attempted to use pattern recognition techniques for the evaluation of strongly overlapping (4 to 12 mV) curves. Fully reversible processes were examined by Sybrandt[61] and Pichler.[62] The examinations relate to curves obtained by stationary electrode polarography (SEP). Both the Linear Learning Machine (LLM) and the k-Nearest Neighbor (kNN) algorithms were stated to be suitable for classification with an accuracy higher than 90%.

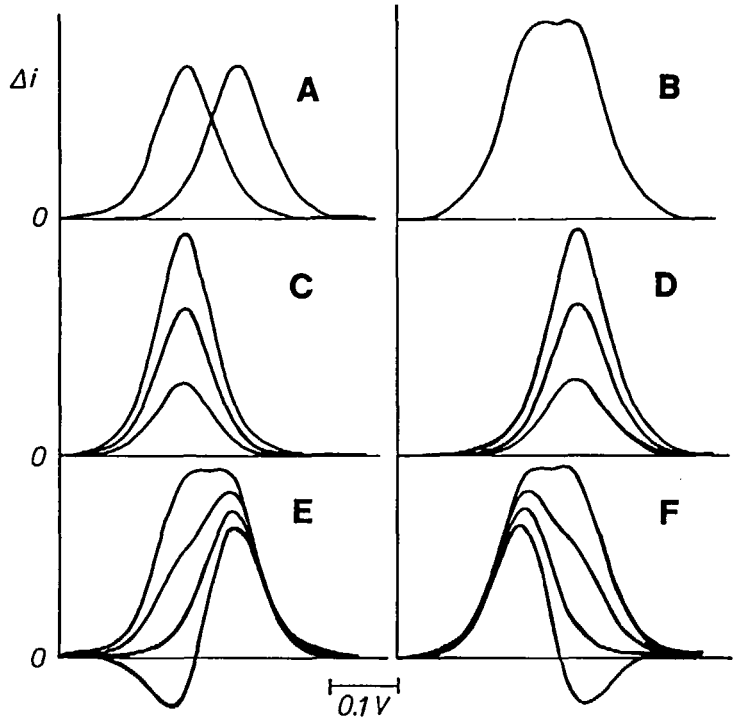

FIGURE 11. Simulated differential pulse polarographic curves showing the determination of two reversibly reduced species, a and b, of equal concentration, according to Bond and Grabaric.[58] $n_a = n_b = 1$; E = −25 mV; drop time = 0.5 sec; δ = 40 msec; separation in $E_{1/2}$ = 75 mV. (A) Polarograms of individual components, a and b. (B) Polarogram actually recorded /a plus b/. (C and D) Addition of a and b to blank, respectively. (E) Determination of b (I-E) curves observed after subtraction of increasing concentrations of a. (F) Determination of a (I-E) curves observed after subtraction of increasing concentrations of b.

Thomas and Perone[63] extended their theoretical investigations for quasi-reversible and irreversible processes and concluded that when applying the kNN approach, the accuracy is higher than 90%, while in the case of LLM, the results seemed to be considerably unfavorable. The analysis of curves mixed with generated noise also was exècuted, and it was found that the separation can be done even in this case by kNN algorithm applying either the Fast Fourier Transformation (FFT) or the SEP theory,* assuming that the noisy curves have previously been subjected to Fourier filtering. The results suggested that for processing the experimental SEP data the FFT-kNN approach is the most promising.

Thomas and De Palma[64] justified their earlier results[63] with the identification of polarographic curves (SEP) of one- and two-component mixtures, containing various metal ions and anions, respectively. None of the earlier methods alone was suitable for solving the task. The best results could be achieved by analysis Leave-One-Out (LOO) (applying kNN approach).

De Palma and Perone[65] improved the earlier On-Line Pattern Recognition method

* Different curves were calculated for the case of different α, η, Ψ (reversibility factor according to Shain) values and different concentration ratios and peak separation. From these various data supposed to be characteristic (SEP features) e.g., (Δ E at 75%) i_p)/Δ E at 80% i_p), i_{p_1}/i_{p_2} (first derivative) have been calculated.

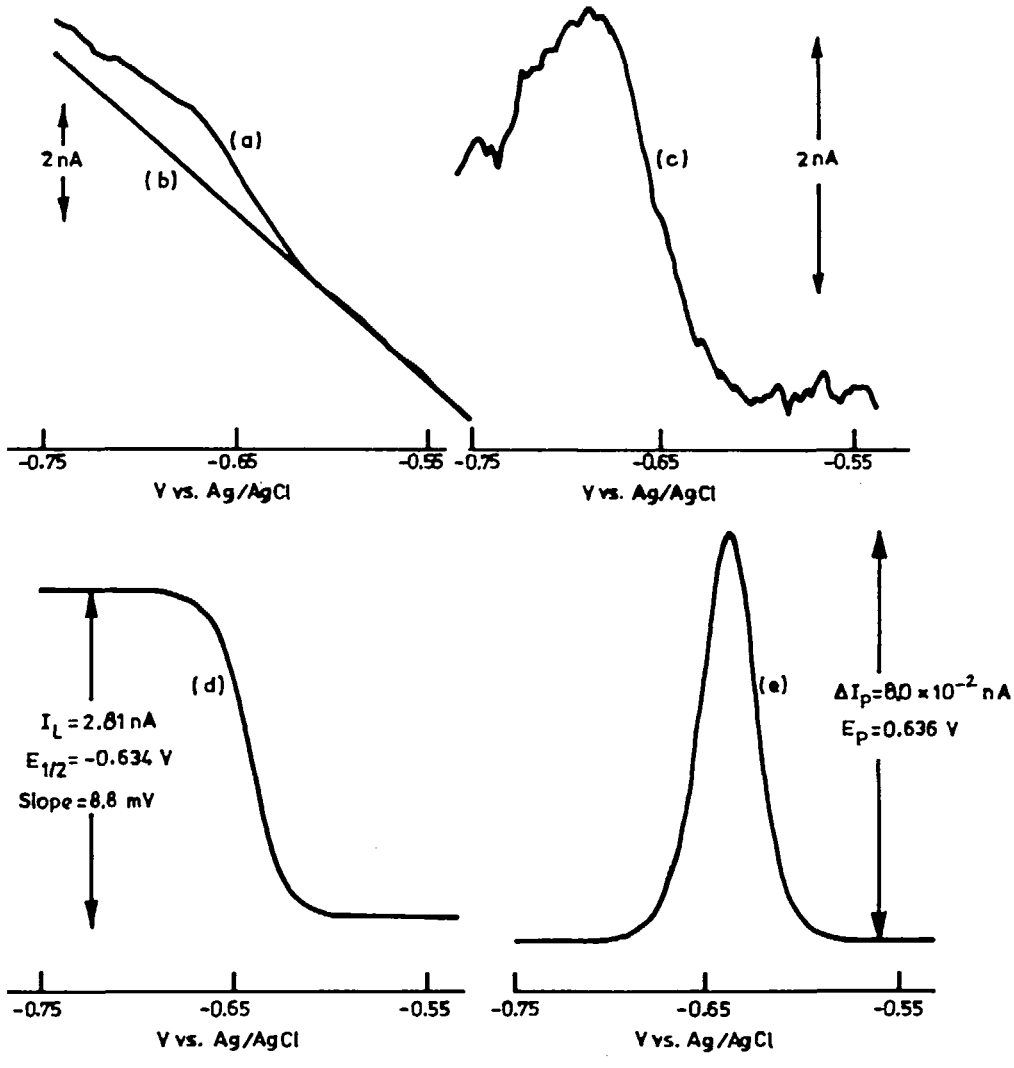

FIGURE 12. Evaluation of pseudo-derivative d.c. polarogram according to Bond and Grabaric[66] (a) d.c. polarogram including background current; (b) linear extrapolation of background current; (c) d.c. polarogram after subtraction of background current; (d) smoothed d.c. polarogram based on all data points; (e) pseudo-derivative d.c. polarogram after all data points have been used in smoothing routine.

used for the identification of strongly overlapping voltammetric curves (<10 mV). In contrast to previous work, synthetic data were also applied in addition to real ones in the course of the identification procedure.

Bond and Grabaric,[66] in their work published in 1978, present a good example of how often the basic methods (simple dc) can become an approach nearly as good as the most up-to-date polarographic methods, with the help of digital data acquisition and computer technique. They developed high-performance polarographic equipment by connecting a polarograph (PAR, Model 174®), through appropriate accessories (AR-11 real-time analog subsystem with programmable real-time clock and A/D converter and DR-11 general purpose interface) to a minicomputer (PDP 11/10, Digital Equipment Corporation®). Applicability and high performance of numerical methods elaborated for the evaluation of dc and normal pulse polarograms recorded by the equipment are

demonstrated by several examples. The result of different steps of the evaluation of dc polarogram according to their method, in the case of cadmium sample solution of low concentration, is shown in Figure 12. The polarogram can be seen on curve a. The residual current correction is made by subtracting the extrapolated values of curve b, which is a line fitted to the initial residual current section of curve a. Curve c demonstrates the corrected polarogram. The next step is the smoothing by curve fitting. Based on the estimated initial data, the computer fits by an approaching calculation the corrected results (curve c) to the general equation describing the polarographic wave:

$$E = E_{1/2} + K \ln (i_l - i)/i \qquad (3)$$

K = constant, $E_{1/2}$ = halfwave potential, i_l = limiting current, and i = instantaneous current.

On the basis of the smoothed polarogram obtained by fitting (curve d), the computer prepares a pseudo-derivative dc polarogram (curve e) ($\Delta i - E_{\Delta E-\text{constant}}$). This method is suitable for preparing a well-evaluable pseudo-derivative normal pulse polarogram from a normal pulse polarogram also even in the case of a cadmium solution of 10^{-7} *M* concentration.

In the case of an unknown matrix, this method of background current correction is, presumably, preferable to the separate recording and subtraction of the blank (background electrolyte). Limitations of applicability of the curve fitting smoothing method are obvious. In the case of processes other than diffusion and in the case of overlapping waves, the simple equation cannot describe the polarogram; thus, its application is deficient. Accordingly, the approach can be used only with limitations.

Perone and co-workers[67] reported on a semiautomatic, fast-sweep derivative polarographic system, where data acquisition and processing are done with a computer connected to the electroanalytical unit. Computerized data processing is preceded by data reduction performed by analog formation of the second derivative of the data. The computerized data averaging method increases the sensitivity of the technique by one order of magnitude at least. The voltammetric measuring device connected to the digital data collector enables us to conveniently study the effect of the various data manipulations upon voltammetric analysis on the same set of data. Bond[68] utilized the above possibility by connecting a Polarographic Analyzer® PAR 174 to a minicomputer, type PDP-11. With this set-up he made comparative analyses studying the capability of various methods: raw d.c. linear voltammetry, d.c. voltammetry using multiple linear potential sweep and data averaging, d.c. method with background correction, semi-integral transformation, curve-fitting semi-integral formation applying the least square method, the semi-differential voltammogram, formation of d.c. differential, and some other a.c. voltammetric analytical approaches. Bond also reported the limitations of data-manipulation methods for the examinations mentioned above.

Approaches using the d.c. measuring technique and optimum measuring conditions resulted in almost identical 5×10^{-7} to 2×10^{-2} mol/ℓ measuring range for the cadmium model solution. At the same time, however, the more advanced techniques, other than d.c., ensuring more favorable signal-to-noise ratio, gave considerably lower measuring limits without any mathematical "trick".

According to expectations, the results obtained confirmed the deterministic role of the measuring technique. At the same time, however, some favorable features of data manipulation methods used in the d.c. technique have also presented themselves in the course of comparative studies.

For measuring devices with an on-line computer connection, it is usually advantageous if the computer also controls the measuring process itself. Namely, in this case, a flexible

measuring program can be used, and on the basis of measured results a feedback interactive operation is possible during the measurement.

In the majority of the polarographic, voltammetric analytical procedures, comparative analytical results can be obtained only by relatively similar measuring programs and, furthermore, the program generators suitable for preparing polarograms must be highly flexible. Due to these facts, in common polarographic practice, the process control function of the computer is of little importance compared to the data handling. In spite of this, some fully computer-controlled (measuring and evaluation) analytical methods are also known.

D. Automated Polarographic Systems

Bos[69] constructed a "computer polarograph" using a relatively low-performance computer (PDP 11/20®; Digital Equipment Corp., 8 K words 16 bits). The scheme of the device is shown in Figure 13 (ASR 33 teletype®; Dectope® unit, TU56; analog to digital conversion subsystem, ADO1; DA conversion subsystem, AA 11D; DLT 1, drop life timer). To operate the polarograph, the computer runs two tasks separated in time according to two programs. One of the tasks is the control of acquiring the response signal. In the course of this the functions are as follows:

1. To adjust the indicator electrode potential to a proper value when starting the measurement and to change it according to the appropriate program
2. To measure and store the current-time relationship with proper accuracy
3. To synchronize the time-interval of current measurement and mercury drop life
4. To give a trigger signal for the hammer to dislodge the mercury drop

The flow chart of a program for preparing an easy-to-use test polarogram (sampled DC) is shown in Figure 14 together with the symbols used.

In the case of the above-mentioned instrument, the other task of the computer is the evaluation of the polarograms obtained. The flow chart of the computer program including the calculation of curve-smoothing and curve-fitting constants can be seen in Figure 15. The memory of the microcomputer at disposal was not sufficient to simultaneously run the two programs and store the data. Therefore, the evaluating program was fed in only after recording, but this solution is quite inconvenient. The authors give an account of their practical experiences obtained in the course of testing several evaluation methods, and they succeeded in elaborating a relatively short computer program.

Kryger et al.[70] developed a universal computerized automatic measuring system suitable for the examination of electroanalytical measuring techniques with electrolysis. The block diagram of the system is shown in Figure 16. The device is built around a fairly high-performance computer (RC 4000, disposing over a memory of 48 K 24 bit words and connected to a 2M disc memory).

The measuring system contains every function usually necessary for a computer-controlled analytical method: analog and digital inputs and on/off relays of TTL and of 220 V. The potentiostat of the voltammetric unit performs an electrode potential-time program determined by the computer. Thus programs of almost arbitrary shapes can be used, e.g., programs consisting of linear sections, containing short superimposed pulses of given frequency and amplitude can be applied in a single-shot mode or in repetitive cycles of a selected number. The instantaneous value of the current flowing between the working and the counter electrode is measured by the voltammetric unit according to a given program controlled by the computer. Data obtained are stored and evaluated by the computer. Functions either measured directly or optionally transformed can be

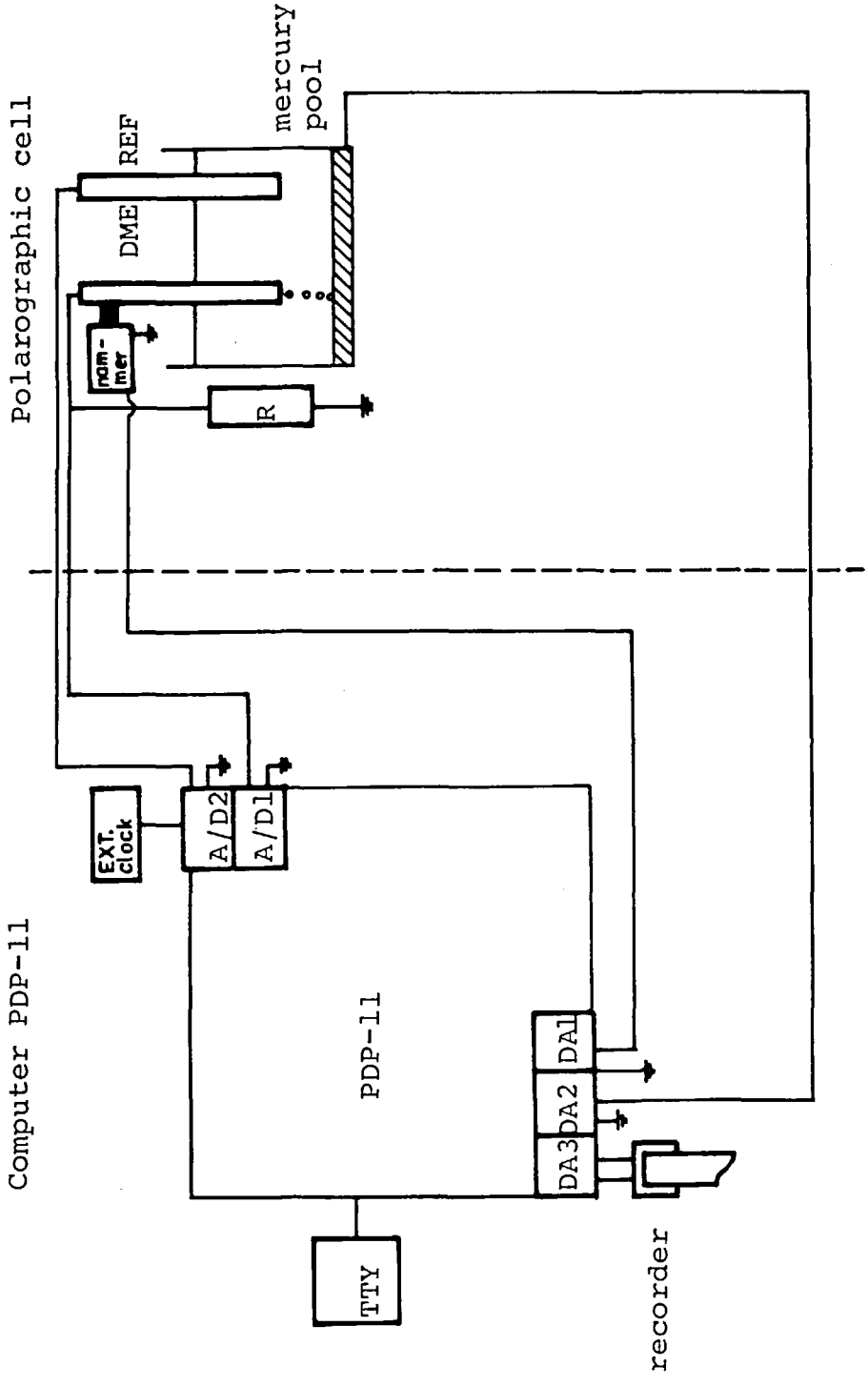

FIGURE 13. "Computer polarograph" according to Bos.[69]

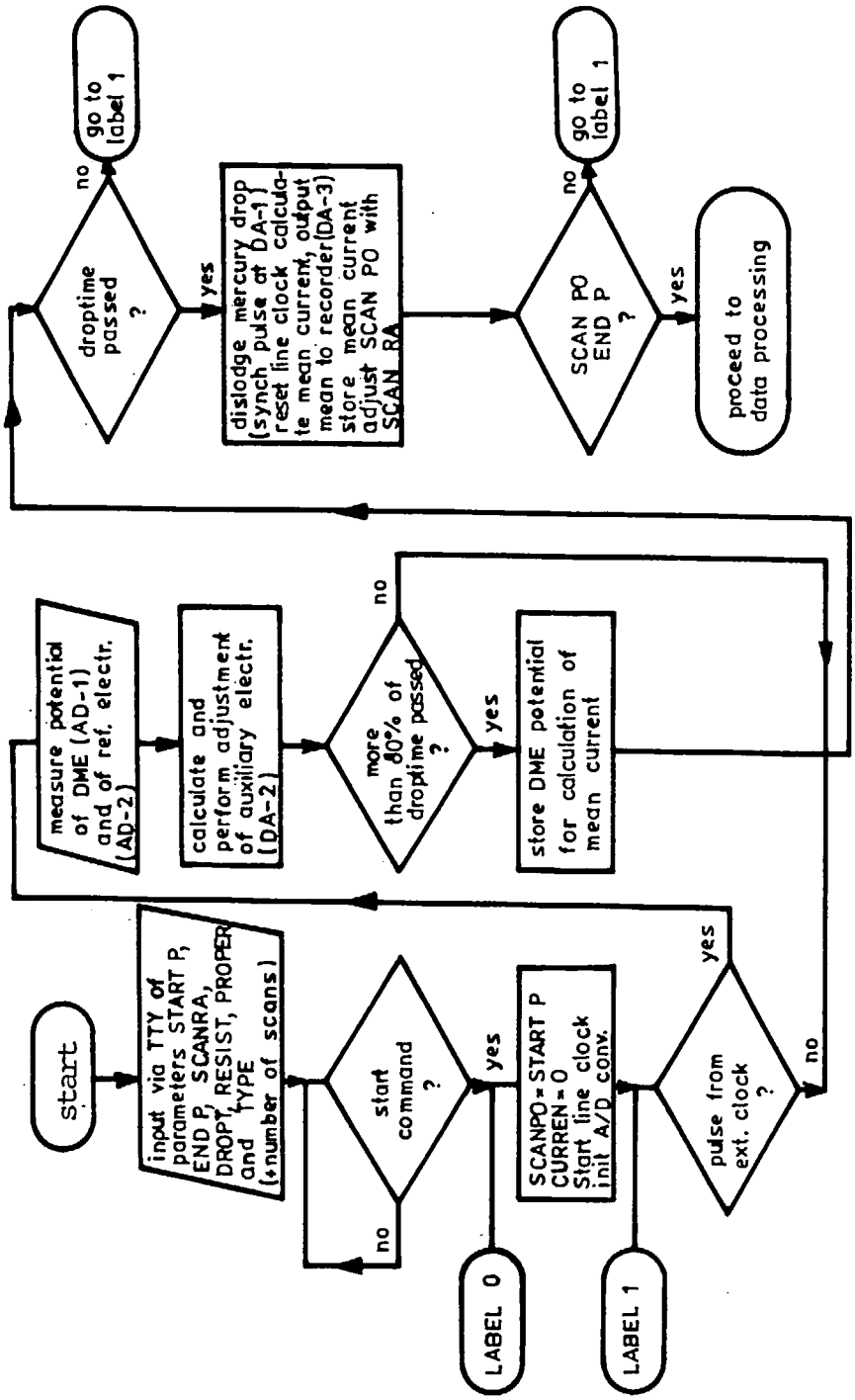

FIGURE 14. Flow diagram of program for ditigal control of polarography according to Bos.[69] Symbols used in flow chart of computer programs — CURREN: measured cell current; DA: Digital to Analog Converter; DROPT: mercury drop time; ENDP: potential of end of scan; NOPOL: number of polarograms to be recorded; PROPOR: amplification factor in IR compensation circuit (can be 1); RESIST: value of current measuring resistor; SCANRA: increment of decrement of potential of DME per drop time; SCANPO: value of potential of DME versus reference electrode; STARTP: potential of start of scan; POTDME: potential of dropping mercury electrode; POTREF: potential of reference electrode; TYPE: Type of measurement, viz. P = single scan, V = single scan + data processing, S = multiple scan + data processing for each scan; $E_{1/2}$: halfwave potential; i_d: diffusion limiting current.

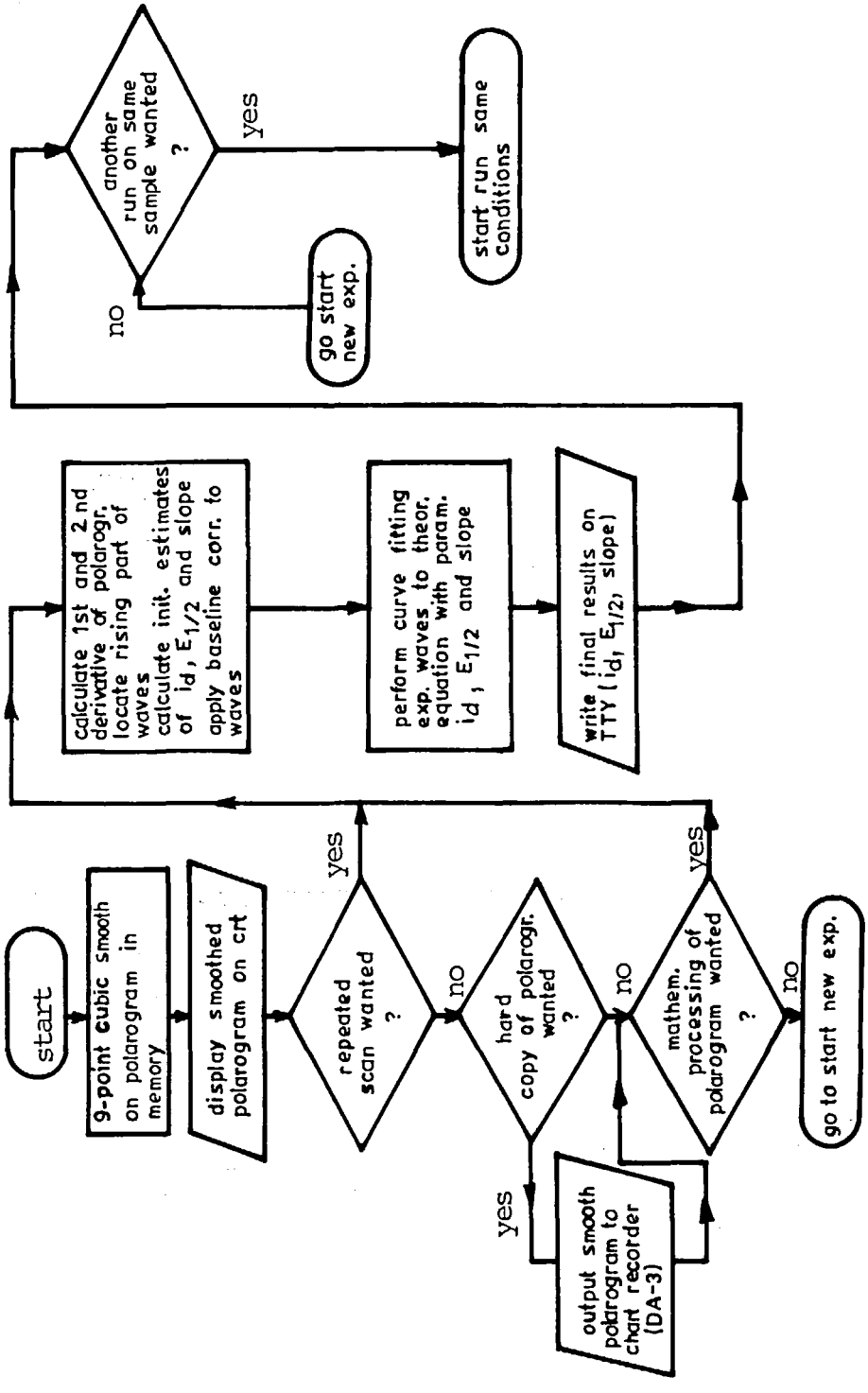

FIGURE 15. Flow chart of program for processing polarographic data according to Bos.[69]

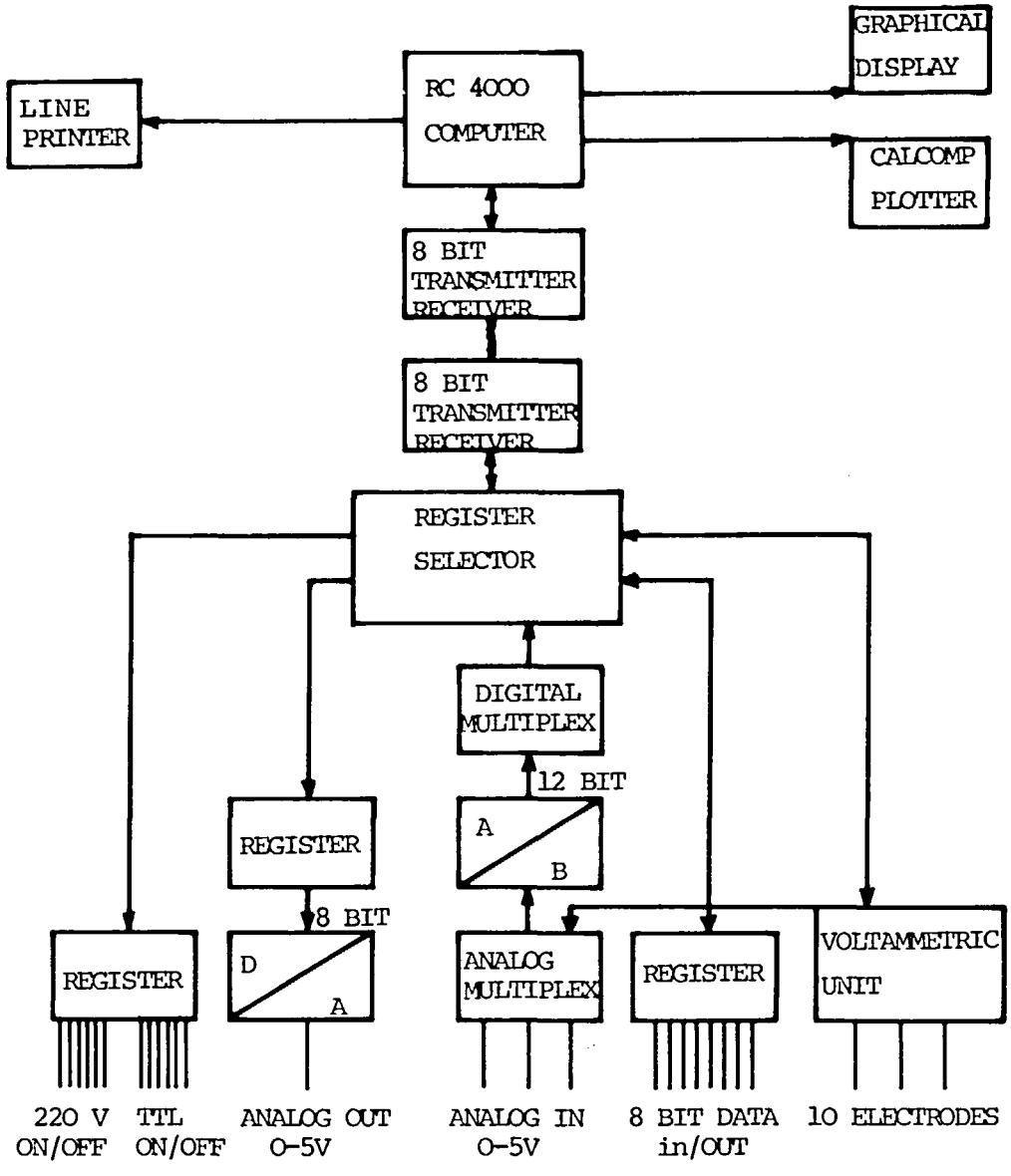

FIGURE 16. Block diagram of the universal computerized automatic measuring system developed by Kryger et al.[70]

visualized graphically on a Tektronix® 4012 display. The use of this instrument is simplified by the fact that it is programmable with a high-level language (ALGOL). The program parts written in assembler language (SLANG) controlling the rapid data handling processes can be called from the ALGOL programs as subroutines.

This measuring system is, obviously, well applicable in several fields of electroanalysis in a wide spectrum of voltammetric measurements, beginning with the simple polarographic examinations up to differential pulse anodic stripping voltammetry. The latter approach is presented by the authors in the first part of their work,[70] while the second part[71] deals with experiences gained in the course of automating the multiscanning and background subtraction stripping methods. According to the

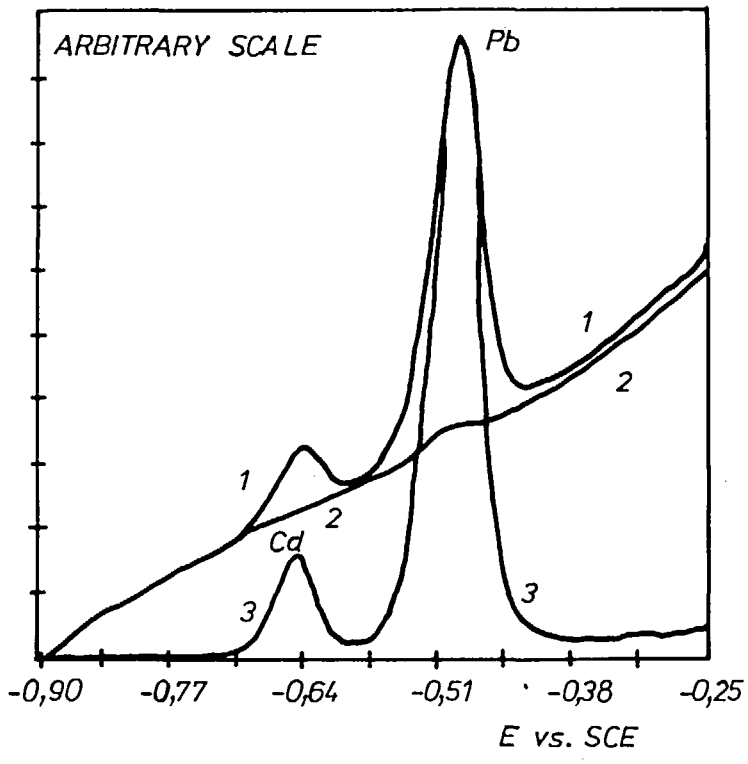

FIGURE 17. The sum of currents from 40 analytical scans (curve 1) and from 40 background scans (curve 2) and the difference between these sums (curve 3) (scan time 0.2 sec), according to Kryger and Jagner.[71]

automatic measuring program in a stirred solution containing mercury nitrate, deaerated by bubbling an inert gas through the solution, a mercury film is deposited electrically upon the surface of a glassy carbon electrode. Then the sample solution (Cd, Pb containing solution) is introduced into the measuring cell. A reduction potential is applied for a certain time interval (−1.3 V; 2 min), and the metals to be determined are enriched at the surface of working electrode, as amalgams. Then, according to the practice of stripping analysis in the measuring cell, the stirring of the solution and bubbling of the inert gas are stopped and linear potential scanning is applied between values −0.9 V to 0.2—0.3 V, increasing in a positive direction and lasting for 0.2 to 0.5 sec. Following this, the program runs a reduction step for 1 sec at a potential −1.25 V and after this, again a scanning step. Thus ions stripped and remaining in the diffusion layer are repeatedly reduced. Repeating the scanning and reduction cycles several times (20 to 40), the computer records the current intensity data measured during scanning and accumulates the data. Following the data collection, the glassy carbon electrode containing the mercury film is rotated and its potential kept at −0.01 V for a few seconds. Thus, ions to be determined leave both the mercury film and the diffusion layer. Repeating the scanning-reducing part of the measuring cycle as many times as done previously, the computer accumulates the background current intensity values. In the case of this multiscanning stripping polarogram corrected with the background value, the signal-to-noise ratio is very favorable; this is shown by Figure 17. The measuring sytem and program allow analyses with high sensitivity (less than 1 ppb for Cd and Pb can be detected) to be performed.

The final step of the voltammogram recording program is to remove the mercury film from the glassy carbon electrode surface. Recording of a new voltammogram begins with the repeated deposition of the mercury film, so the electrode surface is in an approximately similar state in the subsequent measurements.

The measuring instrument used together with the multiple scanning anodic stripping method proved to be applicable for the concentration measurement of polarographically active metal ions present in sea water.[72]

Brown and Kowalski[73] described a new minicomputer-controlled anodic stripping voltammetric technique. The main parts of the apparatus are the following: home-made computer controllable potentiostat, general purpose interface, and a Digital Equipment Corporation® PDP 11/05 GT 40 minicomputer equipped with 24 K core memory and hardware arithmetic capability. The technique uses differential voltammetry at one electrode and a rapid data averaging algorithm. With these, a signal-to-noise ratio better than that of the multiple scanning method mentioned before, an excellent detection limit, and sensitivity and an acceptable reproducibility of <5% could be achieved. The scanning part of the analysis is short. In the method worked out, every experimental step proceeded under program control with parameters selected previously. The program controlled the deposition time and electrode rotation, performed the scan by using a variable point average, and then performed the background scan, again by using point averaging and Fourier® domain digital filtering on request.

Anfält and Strandberg[74] describe a microcomputer system for potentiometric stripping analysis. The potentiometric stripping analysis technique was initiated by Bruckenstein[84,85] and introduced to the analytical practice by Jagner.[75,76] The analysis — primarily of metal ions — is done by concentrating the metals upon the mercury film electrode by electrolysis at constant potential: then they are reoxidized — similarly to the voltammetric stripping analysis. The potential of the working electrode is followed in time in the course of stripping. The time for each metal to be stripped provides information regarding the metal-ion concentration (Figure 18). The advantage of this potentiometric stripping analysis lies in the simplicity of the equipment compared to that used for voltammetric stripping analysis. The stripping may take place by oxygen contained in air, by other oxidizing agents, or electrochemically, which is also facilitated by the system. The microcomputer is expected to control, first of all, the deposition potential and time, but of course other tasks have to be fulfilled, too.

To further improve potentiometric stripping analysis, a single-board computer (INTEL® SBC 80/10) was applied and one more board was also designed to provide for the additional functions. The analog section of the equipment can be seen in Figure 19, while the block diagram of the system is shown in Figure 20.

With respect to the short history of potentiometric stripping analysis, the optimal analytical conditions have not been fully explored. This is why authors paid special attention to the suitable flexibility of the measuring system. To meet this requirement a small integer-based BASIC was chosen from the INTEL user library; this has been written by Li Chen Wang and modified to 8080 code by Rauskolb.

The program controlling the analysis is similarly divided into sections corresponding to the analytical process itself. The parameters are fed in, then the potentiostat is put into use (as a matter of fact, it is essentially not a real potentiostat because the computer controls the potential by software). When the time of electrolysis has expired, the electrodes (working and reference) are disconnected from the voltage source and collection and processing of electrode potential data start.

Reporting on experiences with this measuring system, authors draw attention to some general points of view concerning the automation of analytical instruments. In potentiometric stripping analysis the integration of the micro-computer into the instrument proved to be very advantageous. The computer is helpful not only in

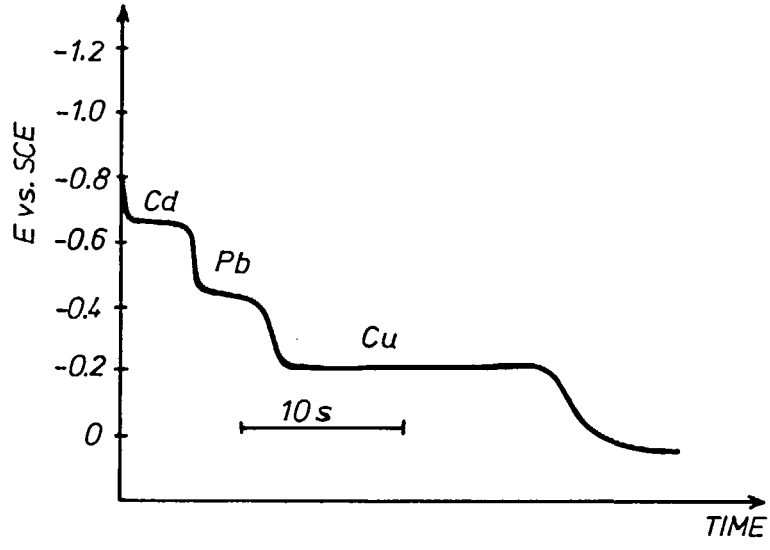

FIGURE 18. Electrode potential vs. time curve obtained by potentiometric stripping analysis of a cadmium, lead, and copper containing solution, according to Anfält and Strandberg.[74]

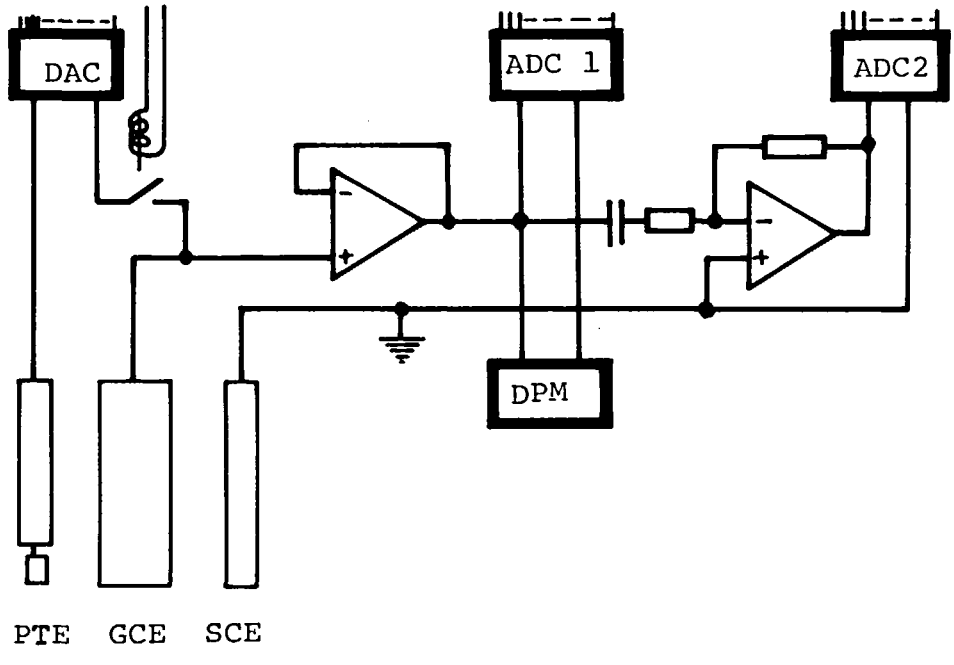

FIGURE 19. The analog section of the potentiometric stripping analyzer developed by Anfält and Strandberg.[74]

controlling the steps of the analytical process, but also in evaluating the results either by standard addition method or by calibration curve. Full utilization of all advantages provided by the built-in computer requires the possibility of reprogramming the computer. This conveniently can be effected only in a high level language like BASIC. Many of the commercial instruments are hardly reprogrammable.

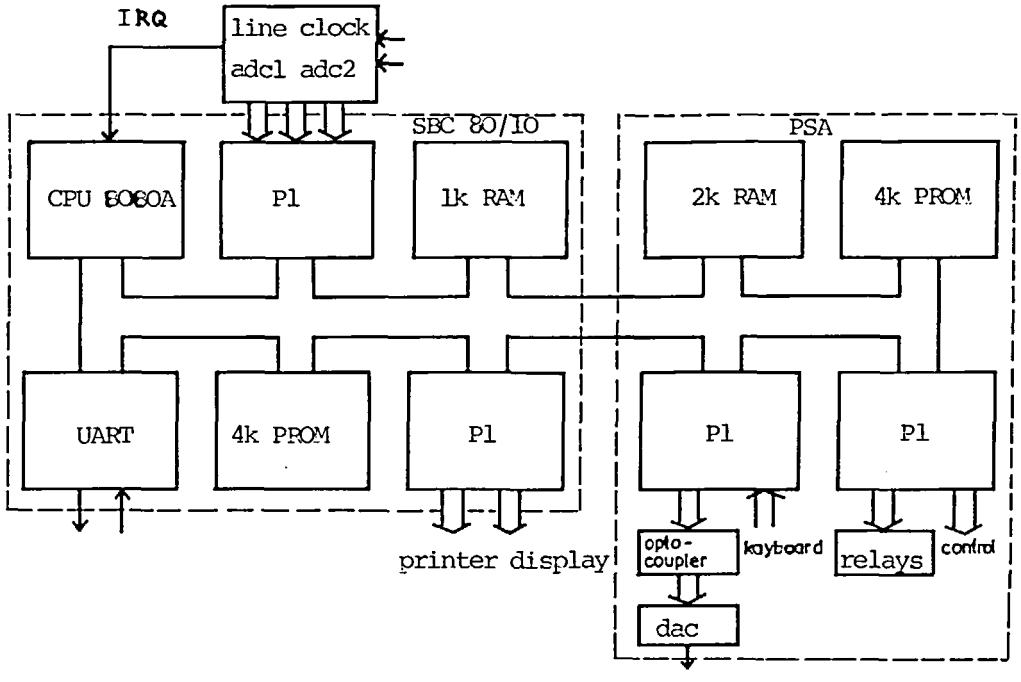

FIGURE 20. Block diagram of the microcomputer system used for potentiometric stripping analysis by Anfält and Strandberg.[74]

In certain voltammetric measurements special advantage can be achieved if a feedback is effected on the basis of the evaluated data. Stripping techniques, where the optimum conditions of preparing the thin film and stripping the metal, highly depend on the actual sample composition. These factors also influence the accuracy of measurement which greatly benefits from the automatic adjustment of parameters.

Perone and co-workers[77] developed a measuring instrument and approach securing the selection of optimum experimental parameters to anodic stripping voltammetry with a hanging mercury electrode. The basic unit of the instrument is a Hewlett-Packard® 2116 (16 K) computer, connected with suitable input-output channels to the analog ramp generator controlling the potentiostat, to the current measuring unit, and to other units controlled by the computer.

To choose the optimum experimental conditions the instrument makes a computer-controlled ASV recording using previously set conditions. On this basis, the location of the peak characteristic of the material to be analyzed, as well as the requested signal-to-noise ratio, are given. Then the computer establishes the needed experimental conditions by making three more recordings under various conditions. Based on the results, the optimum time of electrolysis (accumulation electrolysis time) and the scanning rate are computed. Then, the optimum conditions are used to record the best results. The calculations may, of course, lead to extreme experimental conditions which are beyond the hardware capacity. In this case the analysis should be performed under less strict conditions.

Another example for the feedback-controlled voltammetric measuring program was shown by Perone and co-workers.[59] For obtaining better resolution of overlapping peaks in stationary electrode polarography, a special interrupted sweep experiment was studied. It is based on the observation that if the potential sweep is interrupted at an

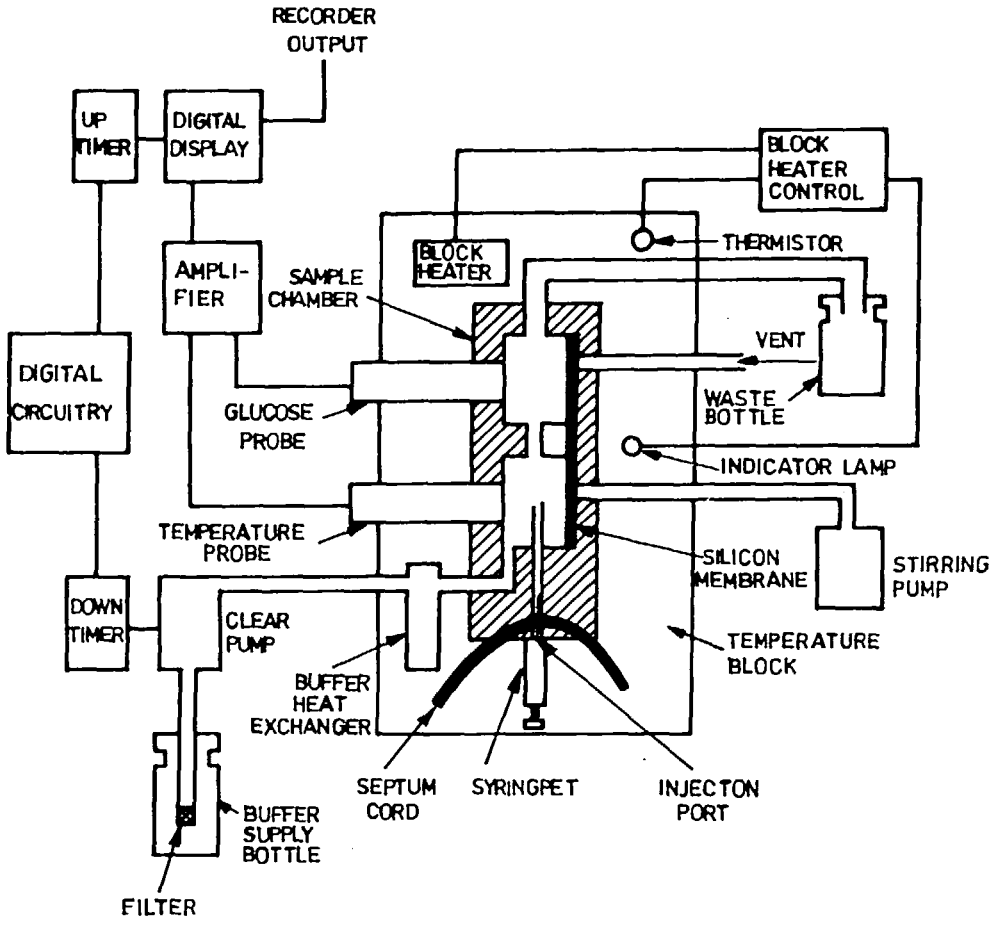

FIGURE 21. Block diagram of the glucose analyzer, Model YSI 23A®, manufactured by Yellow Spring Instruments.

appropriate potential for a given time interval, the diffusion layer can be depleted of the first electrolyzed species. By then continuing the sweep, current peak characteristic for the second component can be obtained with no interference from the first species. To achieve a higher resolution on this basis, two parameters (the potential and length of the interruption) must be determined properly for each case. An interactive computer is a good help for this. Perone's group published convincing results with this sample-oriented, interrupted sweep approach. The schematic diagram of the measuring system is shown in Figure 19. In order to make the evaluation easier, the first and second derivative of the voltammetric current is monitored.

The voltammogram, undoubtedly, implies information regarding the quality of the component participating in the electrode process. The qualitatively characteristic data (half-wave potential, peak potential, half-peak potential), themselves, however, do not make possible the qualitative analytical application of voltammetry. Lately, Perone and co-workers[78] as well as Smith and co-workers,[79] in the course of comparative examinations of voltammograms and polarograms transformed by FFT into frequency domain, observed differences unambiguously characteristic for material quality.

On the basis of these promising works — being initial steps towards the qualitative analytical application of polarography — it can be imagined that polarography will join

the other structure examination methods. Transformed polarograms of various substances — organic molecules — recorded under similar conditions proved to be identifiable with great certainty by using the data bank and an adequate algorithm. Some compounds belonging to certain organic groups having similar structures, exhibited similar voltammetric behavior.

The wide-scale application of polarographic, voltammetric instruments can be expected only if such computer-controlled polarographic equipment will also be commercially available. In general, polarographic instruments are considered to be inexpensive laboratory tools; however, their computerization increases their cost enormously. This contradiction seems to be solved by the price decrease of microelectronic units. In 1973 the microprocessor-controlled polarograph appeared on the instrument market, facilitating practical polarographic analysis and enabling the automation of routine experiments.

Lately, a second generation of microprocessor-controlled equipment has become available. One typical representative is the PAR 384-1® polarograph. This device is capable of performing analytical experiments by applying various polarographic methods, including stripping analysis. Its capacity can be characterized as follows:

- Able to store nine analytical methods, in each case with appropriate blank value correction
- Able to store the data of nine analytical curves and to arbitrarily represent them
- Able to distinguish nine peaks for one scan

Computational functions of the device are

- Automatic concentration calculation either by standard addition or with a calibration curve
- Peak height measuring by tangent fitting
- Background subtraction

The system includes an alphanumerical display, a built-in information capacity of 118,000 bit (by building in micro floppy disks), a stationary-dropping mercury electrode, (Model 303), and a digital plotter.

Similar computerized polarographs are manufactured by several other companies, e.g., SOLEA TACUSSEL (Model TAC 2000®), and the development by others of such kinds of instruments is on the way.[80-82]

In addition to the above-mentioned, general-purpose instruments, some other automated special voltammetric instruments are also in commerce. The following are mentioned as examples: the enzyme electrode glycose analyzer manufactured by Yellow Springs Instruments (YSI Model 23A®), Automatic Trace Metal Analyzer® of the Mitsubishi Chemical Ind., and the new Stripping Analyzer® produced by Tecator and Radiometer companies.

Figure 21 shows the block diagram of the YSI Model 23A® amperometric glucose analyzer. The apparatus detects the hydrogen peroxide formed in the glucose oxidase enzyme containing reaction layer of the sensor. As is obvious from the figure, the apparatus contains relatively simple electronics. Regardless of this, it provides a convenient, relatively fast way of analyzing small volumes (25 $\mu\ell$) of plasma and full blood samples. A similar function is provided by the Glukometer (GKM 01® developed by Scheller and co-workers[83] and manufactured by ZWG (Berlin, G.D.R.). The apparatus determines the glucose concentration using the first-time derivative of the voltammetric current-time transient.

Comprehensively, the following can be said in connection with the polarographic application of digital computers:

1. Several advantages are obtained by utilizing the possibilities of digital data processing. Background correction, data averaging based on data accumulation, curve smoothing and noise filtering are most widely used; competitiveness and capability of polarography are augmented by automation.
2. More complex preliminary mathematical examination of data processing suggests novel applications of voltammetry.
3. The computer-controlled measuring program, i.e., the analysis conditions, can be modified for optimum performance during operation; the feed-back program control can, however, scarcely be considered as a routine polarographic task on earlier instruments.
4. The effective application of polarographic and voltammetric techniques for non-routine samples requires a measuring system where the qualified analyst has an active part in controlling the measurement and in evaluating the results. The human work aspect can be replaced in mechanical, tedious operations.
5. More developed voltammetric techniques usually cannot be replaced by computer "tricks" on data from simpler methods. To put it another way, the use of computers can not make superfluous the application of highly sensitive voltammetric techniques.

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