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#### CONTINUTATION OF BLOCK 20. ABSTRACT

multiple ion selective electrodes are described. Modification and extension of the current hardware and software to permit automation of other potentiometric methods are discussed.

The computer-based systems described bave ranged from a relativaly inflextable single-task potentiomatric titration system (3), to an require multitask system allowing a very nigh degree of interaction between computer and user (5). From the standpoint of either the routine user of 15Es, who is interested in succenting analyses currently done manually, or the researcher to the field of 15E development who is interacted in efficient and convenient evaluation of either new ion selective sensors or new methodology, nearly all of the systems described, thus far, suffer from one or both of the following disadvantages.

The first disadvantage is expense. Systems that have had sufficient computation ability to accomplish, for example, Gran type (5, 6, 7) or standard addition (4, 8) analysis, have been bised on minicomputers which are still very expensive (50,000 to 520,000). For this reason, incorporation of a mini-

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#### INTRODUCTION

A number of examples of computer automation of instrumentation used with ion selective electrodes (ISEs) have appeared in the biterature (1 - 9). The computer-based systems described have ranged from a relatively inflexible single-task potentiometric titration system (3), to an elegant multitask system allowing a very high degree of interaction between computer and user (5). From the standpoint of either the routine user of ISEs, who is interested in automating analyses currently done manually, or the researcher in the field of ISE development who is interested in efficient and convenient evaluation of either new ion selective sensors or new methodology, nearly all of the systems described, thus far, suffer from one or both of the following disadvantages.

The first disadvantage is expense. Systems that have had sufficient computation ability to accomplish, for example, Gran type (5, 6, 7) or standard addition (4, 8) analysis, have been based on minicomputers which are still very expensive (\$8,000 to \$20,000). For this reason, incorporation of a minicomputer into a dedicated potentiometric analysis system is undesirable. If a laboratory minicomputer is already available, mini-micro combinations (2) are an attractive alternative.

The second disadvantage is complexity. The average ISE user may not possess the electronic and computer expertise to assemble a system capable of meeting analytical demands. This problem is, once again, largely associated with the use of a minicomputer in that due to the total system approach to minicomputer construction, interfacing the computer to external devices is a relatively complex process. This problem is frequently made even more difficult by the need to extend existing input/output (I/O) capabilities through multiplexing.

2

CONTINUTATION OF BLOCK 20. ABSTRACT

Microcomputers offer distinct advantages over minicomputers with regard to both cost and complexity. Microcomputers and associated supporting hardware are quite inexpensive, making incorporation into dedicated instrumentation very desirable. Furthermore, because of the modular approach to microcomputer architecture, construction of an analytical system based on a microcomputer is surprisingly easy. Traditionally, microcomputers suffer from lack of software support, however, making high level mathematical manipulations and computeruser interaction very difficult. For this reason, instrumentation based on stand-alone microcomputers described thus far have lacked power and versatility (1, 3).

This paper describes a novel microcomputer-based potentiometric analysis system that incorporates the cost and simplicity advantages of the microcomputer with the high level software capabilities associated with minicomputers. This is made possible through the use of a new computer language, CONVERS (10). Illustrative applications of this system to endpoint determination in potentiometric titrations and fully automated generation of ISE calibration data are presented.

the necessary calculations. In the single ADC algorithm, the computer holds the necessary calculations, in the single ADC algorithm, the computer holds the necessary calculations, frees the meter, waits three seconds and ropes LATMAMINARY.

<u>Electronic Measurements</u>. An Orion 801A digital pH-milivolt meter was used to measure electrode potentials. When in the pH mode, this meter can measure from pH.0.000 to pH 13.999 in 0.001 pH unit increments. When in the millivolt (mv) mode, it can measure potentials from +1999.9 mv to -1999.9 mv in 0.1 mv increments. Interfacing this device to the computer is accomplished through a convenient TTL-compatible interface tab.

The meter is used in conjunction with an electrode multiplexer similar to that described by Zipper, et. al. (8). This device can switch up to six

different electrodes to the meter either manually via a set of front panel switches or under computer control.

Since Orion does not supply the user with information regarding the analog to digital conversion (ADC) frequency or the noise rejection capability of the 801 meter, these parameters were determined experimentally. The ADC frequency was determined by observing the print gate frequency (interface tab pin 16) on an oscilloscope. The noise rejection capability was evaluated by determining the standard deviation of the digitized signal when a constant (but undoubtedly noisy) analog signal was presented to the meter. An Orion fluoride (94-09) ISE in conjunction with a double junction (Thomas 4092-H10) reference electrode (0.1M KCl outer solution) was used to generate the analog signal. The measuring solution was 0.5M NAF maintained at  $25^{\circ}$ C  $\pm$  0.1°C. The electrodes were immersed in this solution one hour prior to measurement to ensure that a constant EMF was being produced. The measuring solution was covered to prevent evaporative losses.

Standard deviations for both single and averaged ADCs were calculated. Simple CONVERS computer algorithms were used to generate the data and perform the necessary calculations. In the single ADC algorithm, the computer holds the meter, samples, frees the meter, waits three seconds and repeats the process. Twenty readings are taken and used to calculate a standard deviation. Ten standard deviations are calculated and averaged during an analysis. In the averaging algorithm, the computer obtains a number of ADCs at the maximum ADC frequency. This is done by continuously checking the print gate and sampling once after each low-high transition (low = busy state). These ADCs are then averaged to give a reading. As before, twenty readings are used to calculate a standard deviation and ten standard deviations are calculated and averaged per analysis. Buret System. A Mettler DV10 digital buret drive with 10 ml buret (DV101) was used. The accuracy of the buret was determined gravimetrically with water. The buret was found to be accurate to about 0.1% over the entire volume range. The buret tip was submerged in the measuring solution throughout both the titrimetric and calibration experiments. The buret is triggered by a pulse train from the computer. Each pulse causes the buret to deliver 1 µL of titrant. The maximum pulsing frequency is 166 Hz. An interface board output strobe was used in conjunction with a 74121 monostable integrated circuit chip to provide the required pulse train. The magnetic stirrer is turned on and off by a TTL triggerable relay circuit. The relay switches 120V AC to the stirrer.

<u>Computer and Associated Hardware</u>. A schematic diagram of the computer and associated hardware is shown in Figure 1. All components except the electrode multiplexer are commercially available. The computer is an IMSAI 8080 microcomputer kit (IMSAI Manufacturing, San Leandro, CA) equipped with 24K of static memory (Jade Computer Products, Hawthrone, CA). All interfacing is done through Processor Technology (Emeryville, CA) 3P+S I/O boards which fit directly into the computer's S-100 motherboard. Two 3P+S boards are used. The floppy disk drive is a North Star (Berkeley, CA) MDS-A. The disk drive control board is also S-100 compatible. The X-Y recorder is a Hewlitt-Packard 7001A.

<u>Programming</u>. All programming was done in a recently developed computer language, CONVERS, (10). This language is based on an interpretive compiler and combines the conversational and easy debugging characteristics of an interpreter type language (for example, BASIC) with the speed associated with a compiler type language (such as FORTRAN). In addition, I/O control and high level arithmetic routines are provided. The high level I/O routines are a particularly attractive feature of this language in that they obviate the need

for assembly language subroutines for I/O operations.

To demonstrate the capabilities of this system, software to locate endpoints in a potentiometric titration and plot out the titration curve and software to calibrate up to six ISEs and plot out the calibration curves was written. Programs were written with the aid of the CONVERS disk operating system (CDOS) and text editor. The CDOS was used for program storage and retrieval. Overlays were used to conserve memory space. For most applications described, 16K of memory was sufficient.

The potentiometric titration program uses routines similar to that described by Christiansen, et. al. (3) to calculate desired titrant increment volume (DTIV) and locate endpoints. DTIV is calculated on the basis of the magnitude of the first derivative of the titration curve. The endpoint is located by calculating the second derivative and extrapolating between the last positive and first negative values. Two slightly different routines were used, one for acid-base titrations in which the meter is used in the pH mode and one for general potentiometric titrations in which the my mode is used. The software quizzes the meter to determine which mode is operative and implements the approriate routine.

A very high degree of computer-user interaction is easily obtained with the CONVERS language. This is evidenced in Figure 2, which shows a typical computer printout from a potentiometric titration (titration of a mixture of acetic and hydrochloric acids with sodium hydroxide). The statements before the equal signs are typed by the computer, the numbers are entered by the user. The concentration entered is in molarity and the sample volume in mL. The points the computer is instructed to take after an endpoint is located allows for detection of multiple endpoints. The titration will cease after the desired number of extra increments are added unless another region of increasing

slope is detected in which case the desired extra increments are added after this additional endpoint has been located.

The drift parameter is entered in mv. The computer will continue sampling the electrodes after an increment has been added until two consecutive readings (separated by 6 seconds) differ by less than this specified amount or until the number of 6 second intervals entered in the next statement has been surpassed. In this case, a maximum drift rate of 0.1 mv per minute and a 1-minute equilibration time were specified. If the electrode drift exceeds these criteria after addition of a particular increment, the computer informs the user and continues with the titration. As indicated in Figure 2, excessive drift was present during this titration after addition of increment number 51.

The maximum and minimum pulses determine the maximum and minimum increments the computer is to add. The maximum increment is added when the algorithm used to calculate increments produces a number greater than the maximum specified and the minimum increment is added when a number smaller than the specified minimum is calculated. For this particular titration, the maximum increment was rather small (70  $\mu$ 1) so that the poorly defined first endpoint corresponding to the concentration of HC1, could be located (see Figure 3). Once this endpoint is located, however, the software changes the maximum increment to 0.3 ml so that the second endpoint may be quickly located.

The final parameter entered specifies how many consecutive negative second derivatives must be calculated before an endpoint is recognized. This safeguards against the possibility of a false endpoint being detected due to the instability of electrode potential often encountered in the region of the endpoint. As indicated in Figure 2, at the end of the titration a report listing the number of endpoints detected, the endpoint volumes and concentrations calculated is printed on the teletype (TTY).

Upon completion of a titration, the user may have the titration curve plotted on the X-Y recorder. This is accomplished by overlaying the CONVERS plot routine. The plot of the data obtained from the titration shown in Figure 2 is shown in Figure 3. The sample number entered for the titration is reproduced on the plot. In addition, a legend for the plot is printed on the TTY. The numerical coordinates in Figures 3 and 6 were hand lettered.

Titrations carried out include titrations of potassium hydrogen phthalate, acetic acid and hydrochloric acids with sodium hydroxide. A Thomas glass electrode (4090-B15) and saturated calomel reference electrode were used.

For ISE calibration experiments, the digital buret is used to create a series of user specified solutions by titrating a stock solution into a blank consisting of either water or a salt solution, whose ionic stnength has been adjusted. The software consists of two programs. In the first program (SOLU-TION-GEN) the user is asked to input a sample number, the number of electrodes to be calibrated, the blank volume (ml), the highest and lowest concentrations desired (molarity), the change in +log concentration desired, the stock solution concentration (molarity) and the minimum and maximum volume increments to be added (pulses). The computer uses this information to calculate how many times the buret must be pulsed to create each of the user specified solutions. This data is printed on the TTY and stored in a memory array. A typical computer printout for SOLUTION-GEN is shown in Figure 4.

The second program (CAL-ISE) may then be overlayed. CAL-ISE uses the data stored by SOLUTION-GEN to calibrate the ISEs. The user is asked to input the maximum tolerable electrode potential drift rate (mv/min), the number of minutes to wait for electrode drift to decay below this specified rate, and a delay time (sec) corresponding to the time the computer is to wait between switching an electrode to the meter and sampling. A simplified flow chart of the

calibration process for two electrodes is shown in Figure 5. As can be seen from Figure 5, sampling continues for each electrode until all electrodes produce two consecutive readings that differ by less than the specified drift rate or until the specified maximum time has elapsed.

At the end of the calibration, the -log concentration-potential data for each electrode is printed on the TTY. In addition, the user is notified during the calibration of those solutions for which satisfactory potential readings could not be obtained. The user may then have the calibration curves plotted on the X-Y recorder by overlaying the plot program.

Calibration data was generated for coated wire ion selective electrodes (CWISEs) of the  $NO_3^-$  and  $ClO_4^-$  type and for the Orion F<sup>-</sup> electrode. The CWISEs were prepared as described elsewhere (11, 12). Potentials were referred to the double junction reference. The outer filling solutions were 0.1M  $NH_4NO_3^$ and 0.1M KCl for the  $ClO_4^-$  and  $NO_3^-$  CWISEs, respectively, and 0.1M KCl for the F<sup>-</sup> ISE. Thermostated (25°C ± 0.1°C) 300 mL beakers were used as sample cells. The beakers were covered during calibration to prevent evaporative losses.

RESULTS AND DISCUSSION

<u>Meter Response</u>. The 801A uses an integrating analog to digital converter (A/D). This type of A/D has excellent noise rejection, which accounts for the great stability of the digital display, however, ADC is relatively slow. Speed of ADC is not an extremely important consideration here, however, in that ISEs are inherently slow devices. The ADC frequency of the 801A was found to be around 5.5 Hz. Use of the meter print gate as a sampling flag, as described in the experimental section, allows for synchronized data transfer from meter to computer at <u>near</u> this frequency.

The noise present after analog to digital conversion was evaluated by

determination of the standard deviation for both single and averaged readings. The standard deviation for a single reading was found to be around  $\pm 0.03$  mv. The standard deviation for a 25 point.average was found to be around  $\pm 0.01$  mv. Increasing the number of points averaged to 50 did not further lower the standard deviation. The decision to use either single point sampling of meter response or an average of multiple points should be made on the basis of precision desired and electrode characteristics. Changes in the sampling routine may be implemented through minor software modifications. For the calibration curve experiments, a 25 point average was used. For titrations, a single point sample was sufficient.

#### Titration Experiments

Results of various acid base titrations are summarized in Table I. Each result represents an average of at least four determinations. As indicated, for all titrations relative precisions of under 0.1% were obtained using the automated titration system. Results of titrations of a mixture of acetic and hydrochloric acids are shown in Table II. Good accuracy and precision was obtained for both the HCl and total acid endpoints. This data demonstrates the power of the endpoint locating algorithm when, as shown in Figure 3, the break in a titration curve (HCl endpoint) is not very pronounced.

#### Calibration Experiments

Calibration curves obtained with the automated system for all electrodes tested were identical to those obtained manually in terms of slope, range of linear response and standard deviation. Calibration curves obtained for four  $C10\frac{10}{4}$  CWISEs, are shown in Figure 6. In this case, solutions ranging from  $10^{-4}$  to  $10^{-2}$ M  $C10\frac{10}{4}$  were created. Water was used as the blank solution.

Due to the limitations in resolution and volume of the digital buret, the calibration curves generated by this method have a maximum concentration

dynamic range of about three orders of magnitude. By varying either the standard concentration or the blank volume, however, any concentration region may be investigated. Hence if the response characteristics of an electrode are desired over a larger concentration range, multiple calibrations, with each examining a different portion of the response curve, may be run.

#### Cost

The approximate costs of the various components used in assemblying this system are shown in Table 3. It is important to note that the cost of the computer and associated hardware is less than one-third of the total system cost. Had a minicomputer with comparable hardware and software capabilities been used, the computer hardware cost would have, at least, tripled and the total system cost doubled. It is also important to note that no software expenses have been included (the CONVERS software system may be obtained free of charge).

#### CONCLUSIONS

A powerful microcomputer-based potentiometric analysis system has been constructed. This system combines the low cost and ease of construction advantages associated with microcomputer-based instrumentation with the high level software capabilities generally only associated with minicomputers. It is the first low cost/high power potentiometric analysis system to be reported and as such should be of great interest to workers involved in both the fundamental and applied aspects of ISE technology.

The ability of the system to locate endpoints in potentiometric titrations and to generate calibration curve data for multiple ISEs has been demonstrated. Other applications such as pKa and metal-ligand formation constant determination, standard addition and linear (Gran) titrations and automated determination of ISE selectivity coefficients could easily be implemented. These extensions would merely entail writing the appropriate CONVERS programs. Furthermore, additional instrumentations, such as carousel type sampling devices or equipment associated with flowing stream potentiometry (2), could easily be added to the system. Such hardware extensions would merely entail purchasing additional I/O boards and connecting the desired devices to these boards. Circuit diagrams of interfaces and source listings of programs are available on request.

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#### ACKNOWLEDGEMENTS

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This work was conducted with financial assistance from the Office of Naval Research.



Figure 1. Schematic disgram of instrumentation.



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NO. ENDPOINTS=0000002 ENDFOINT VOLS. ARE +.193376E+01 +.482602E+01 UNKNOLN CONCS. ARE +.394720E-01 +.985088E-01

Figure 2. Typical computer printout for program TITRATE.



Figure 3. Computer generated plot of titration curve.





28 28 28 C 2857 0( 0)

Figure 4. Typical computer printout for program SOLUTION-GEN.

510015 1.8.53 7.6.6014.6

Figure 5 Simplified flowchart for program CAL-15:

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## Figure 6. Computer generated plot of calibration curves for four $C10_4^-$ coated wire ion selective electrodes.

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### Table II. Precision and accuracy of automated titrations of acetic and hydrochloric acid mixture with NaOH.

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