

AUTOMATION OF POTENTIOMETRIC TITRATION WITH A PERSONAL COMPUTER USING AN IBM COMPATIBLE INTERFACE SYSTEM

Mulugeta Desta*

Department of Chemistry, Addis Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia

(Received October 13, 2001; revised December 22, 2001)

ABSTRACT. An IBM compatible interface card system with infrared source-detector data sampling was designed and tested for automation of potentiometric titrations with personal computers without continuous measurement of the volume of the titrant. The device with other appropriate apparatus and setup was tested for determination of iron(II) samples with potassium dichromate. The automation method developed was tested to the titration of 1.500×10^{-4} M iron(II) sample and gives a reliable result of 1.496×10^{-4} M iron(II) with a relative error of 1.76%.

KEY WORDS: Potentiometric titrations, Automation of potentiometric titrations, Infrared source-detector data sampling, Determination of iron(II) samples

INTRODUCTION

Recent advances in computing technology and related drops in cost of computing capabilities have spawned a new generation of analytical instrumentation [1-3]. The huge development of microelectronics and automation systems is changing the way we work, thus freeing us from tedious, iterative tasks and allowing us to devote our efforts to creative activities. Further more, automation permits us to carry out new types of experiments, such as those requiring acquisition of large amounts of data in a short time, simultaneous control of a large number of parameters, or long time periods for completion.

Before introduction of the microprocessor automatic systems were not flexible [4]. They were designed to accomplish a specific task and usually could not be reused for other purposes. This situation changed dramatically when the microprocessor appeared. Today, most automatic systems are controlled by microprocessors. These complex and inexpensive devices makes possible the acquisition, storage and treatment of an enormous amount of information. The interest of handling large volume of data increases as the development and popularization of analytical instrumentation [5]. On the other hand, microprocessors provide many powerful and flexible ways of achieving full laboratory automation. However, instead of building up automatic system with raw microprocessors, a microprocessor-based system such as computer may be used. Today, automation is largely facilitated by the use of personal computers, which are increasingly more powerful, compact and inexpensive. Also, they can communicate with scientific instruments, experiments and all kinds of devices using standard interfaces and may be programmed using high-level languages [6]. Therefore, potentiometric titration is one of the analytical methods that could be automated with microprocessor based systems or computers.

Potentiometric titration provides data that are more reliable than data from titration that uses chemical indicators and particularly useful with coloured or turbid solutions and for detecting the presence of unsuspected species [4]. Potentiometric titrimetry is also widely used both as a routine analytical method and as one of the most accurate and precise method for the evaluation of stability constants. The latter requires waiting for the electrode to reach equilibrium after each

*Corresponding author. E-mail: chemistry.aau@telecom.net.et

titrant addition before taking measurement. Times as long as several hours are frequently required near the equivalence points (non-buffered regions) and sometimes even over the whole titration (*e.g.* acid-base titration with a glass electrode). This makes the experimental procedures tedious and time consuming and measurements are not always objectively taken. Therefore, potentiometric titrimetry can benefit greatly from automation with personal computers.

Several automatic potentiometric titrators have been marketed during the last decade. They have proved to be very useful in routine tasks but not in research, due to their closed design. Most of them cannot be adapted by the user to a particular requirement of many research tasks [4]. Therefore, here attempts have been made to design and construct an IBM compatible interface card system to automate potentiometric titration without continuous monitoring of volume by just using normal burettes.

EXPERIMENTAL

Experimental setup. The experimental setup is shown in Figure 1. The infrared (IR) emitting diode generates a continuous IR radiation to the IR detector, which is an IR phototransistor. In this case the phototransistor is in conduction state and the voltage at its collector will be low. When the titrant drop passes between the IR source and detector, it interrupts the IR radiation. Then the phototransistor will not be in conducting state or switched off and the voltage at its collector will be high. Since the pulse generated by the titrant drop is not sharp due to the oval shape of the drop, it has to be shaped into a rectangular wave by the Schmitt trigger NAND gate. The output of the Schmitt trigger was a TTL (transistor-transistor-logic) pulse, which was input to the counter (8254). This pulse was used by the computer's CPU (central processing unit) to command the ADC (analog-to-digital-converter) to read electrode potential at the pH meter's recorder output and subsequently convert it into digital value. The pH/mV meter used was Philips PW 9418 analog pH meter. The electrodes used were saturated calomel electrode (SCE) and platinum electrode as a reference and an indicator electrode, respectively.

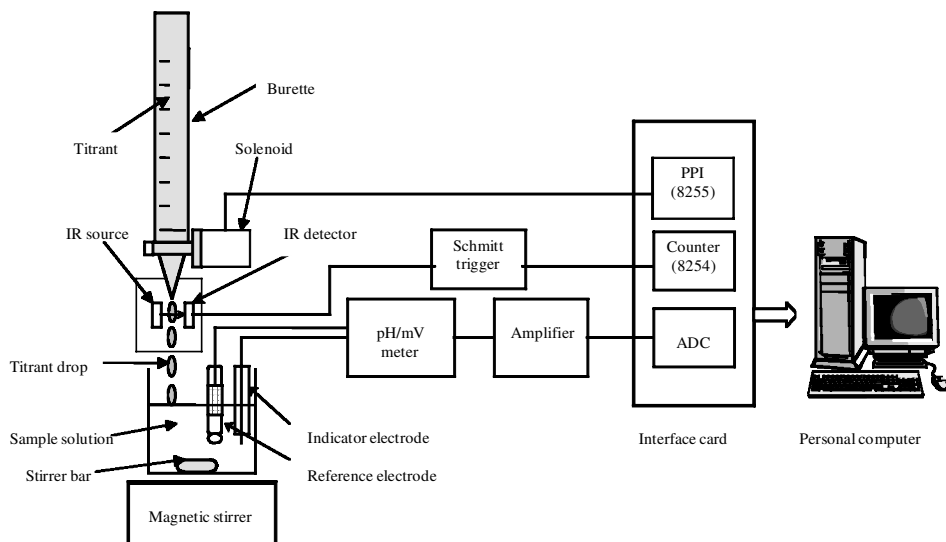


Figure 1. Experimental setup designed for automation of potentiometric titration.

The potential readings were always taken after about one second of delay to allow the titrant completely react with the sample. This is done by a simple delay sub-routine in data acquisition program. The analog potential converted by the ADC is then continuously stored in the computer's hard disk drive. When the equivalence point has passed the data acquisition could be halted by just closing the burettes valve. Then the total volume consumed was manually recorded and used for data analysis by Microcal Origin software.

Data acquisition software. The software used for data sampling and data acquisition from the pH/mV meter to the computer was written in QuickBasic by the author.

Data analysis and graphics. The software used for the analysis of data and graphical presentation was a MicroCal Origin version 4.0. The experimental data, which was in ASCII format, was imported and then plotted either in scatter or line graph form. The graph is plotted in the form of potential against the number or data points. Since the data is taken at equal interval and uniformly proportional to the volume consumed, a new volume axis could be generated easily on the same graph as an upper x-axis. The first and the second derivatives of the titration curves and the exact volume of the equivalence point could be easily read by just placing the cursor. Finally the concentration could be calculated with the normal titration procedure.

Procedure. Known amount (0.50 g) of ammonium iron(II) sulphate (BDH, AnalaR) was dissolved in 100 mL of glass distilled water, 25 mL of this solution was placed in a 250 mL beaker, 25 mL of 2.5 M sulfuric acid and 50 mL of distilled water was added to it [7]. The burette, to which the infrared source-detector system was attached on its tip, was filled with 0.10 M potassium dichromate solution (BDH, AnalaR). For lower concentration experiments both the sample and the titrant were diluted as required. The indicator platinum electrode and reference electrode (SCE) were immersed in the solution, the stirrer was set in motion and the power supply of the drop counter (data sampler) was turned on, then the computer data acquisition program was executed and set ready for reading the electrode potential from the pH meter. The burette valve was then opened to begin the titration process. After the equivalence point had passed, the burette was closed and the computer stops data acquisition automatically. The saved data on computer's hard disk drive was then imported into MicroCal Origin Version 4.0 Software [8] for further analysis and plotting the titration curves.

RESULTS AND DISCUSSION

The IBM prototyping board used for assembling of interfacing components measures 97 mm high by 332 mm long with a 2 by 31 way 2.57 mm pitch double sided, gold plated connector. It is designed to plug into one of the expansion slots in the motherboard of the computer. To simplify the interfacing of the prototype board circuitry to the computer system, on board circuitry is provided to buffer and decode relevant signals. The buffered and decoded signal, that are available on the prototyping are; 8 data bus lines, 1 address decoder line, 5 address lines and one memory write line. The prototyping board is designed to buffer the input/output lines and provide address decoding as recommended by IBM. IBM has allocated addresses in the range of 300 to 31FH for prototyping board devices [9].

The problem encountered when attaching interfaces to the bus of the PC was that of matching the speed of the PC bus cycle with that of the interface designed. It is not uncommon for an interface to operate at a slower data rate than that of what the bus cycle provides for.

The PC system bus is designed such that these problems can be solved [10]. A signal called 'ready' on the system bus, when controlled properly by an interface, can be used to extend the length of a PC bus cycle to match that of a slower interface to half a bus cycle until it is synchronized with an interface cycle (Figure 2).

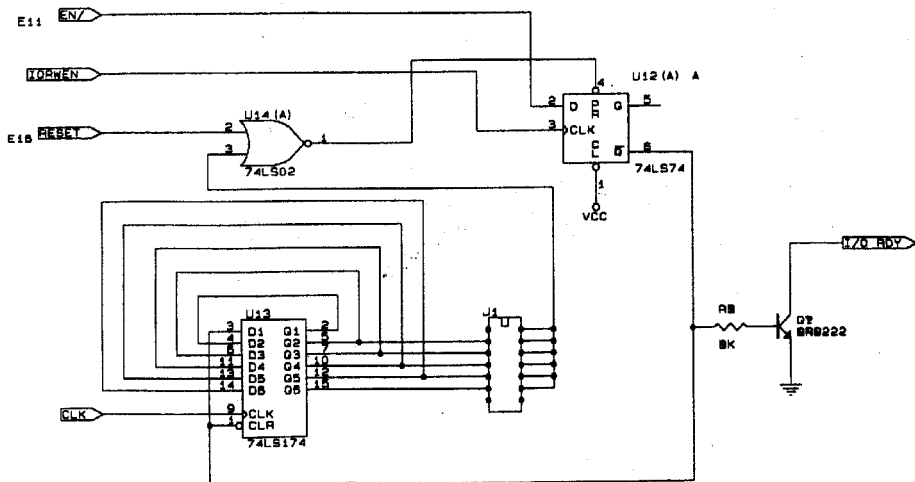


Figure 2. Wait-state generator circuit diagram.

Counter (8254). The counter 8254 provides three independent 16-bit counters each capable of handling clock inputs up to 10 MHz [11]. These counters can be used for event counting, programmable rate generators, square wave generators, binary rate multipliers, complex wave generators, etc. In our experiment of automation of potentiometric titrations, the counter was used as a data sampler for commanding the ADC to convert the electrode potential in to a digital value. When a drop of titrant interrupts the IR sources-detector system, it generate a pulse which will be sharpen by the Schmitt trigger NAND gate (Figure 1) to give sharp edged pulse for the counter to be used as a data sampler signal. In other words it commands the computer to take the potential reading from the pH/mV meters recorder output via the ADC.

Programmable peripheral interface (PPI). The 8255 shown in Figure 3 is a programmable peripheral interface device designed for use in Intel microcomputer systems [12]. It has 24 input-output ports that may be individually programmed in-groups of 12 and three operation modes. Its function is to interface peripheral equipment to the microcomputer system bus. In this automation of potentiometric titration, 8255 together with opto-isolators and solenoids were used for opening and closing of the burette's valve through software command. In other words for starting and stopping the titration process.

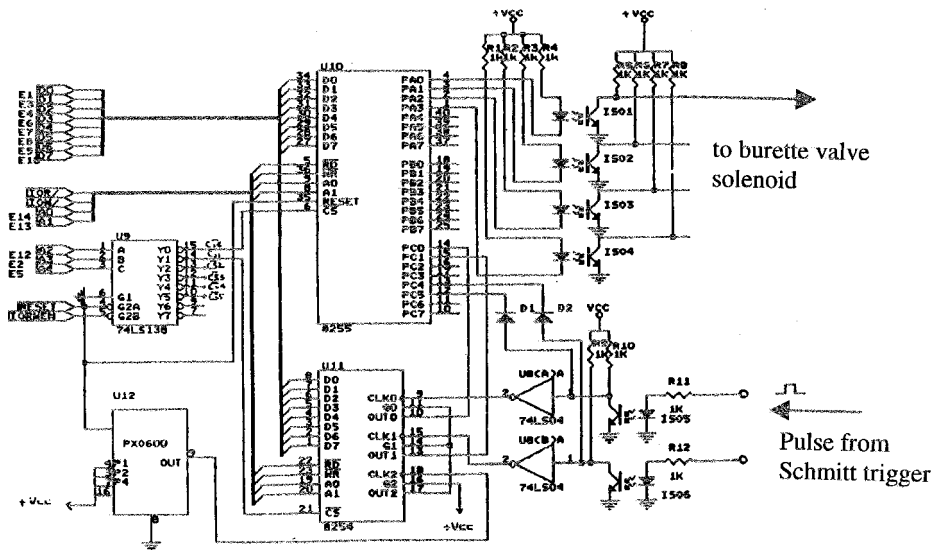


Figure 3. Circuit diagram of the counter (8254) and programmable peripheral interface (PPI) (8255) used for data sampling, counting and controlling.

Analog-to-digital conversion. Much of the information concerning the state of an interface is represented as a voltage that is proportional to some external conditions. Most detectors or transducers in the instruments convert the condition that they are sensing into current or voltage output. The voltage or current cannot be sensed with digital systems. To perform the transformation of a voltage or current level into a digital value an analog-to-digital converter (ADC) is used [13]. When interfacing an analog signal from the instrument to the ADC we have to consider the input range of the device. If the input is too small, we have to amplify the signal using a positive gain operational amplifier. If the input is too large a simple precision resistor-divider can be used. In our case since the recorder output of the pH/mV meter was in the range of 0-100 mV. An amplifier constructed from single operational amplifier was used to amplify the electrode potential signal from the pH/mV meter by a factor of 50 to match the input range of the ADC, which was from -5V to +5V. Therefore, since the electrode potential of any element is within this range the method could be used for other elements as well.

Care had also been taken about the possible offset error introduced by the analog system to the ADC. If the voltage level we are trying to measure is too small offset error will be of concern. Therefore, care had been taken to insure the offset error kept much smaller than the smallest voltage to be measured. Although care had been taken to insure that the ADC does not overload the source and alter the true value being measured. Therefore, to avoid this problem a unity gain operation amplifier in voltage follower configuration, with high input impedance to buffer the input to the ADC was introduced between the pH meter output and the ADC input.

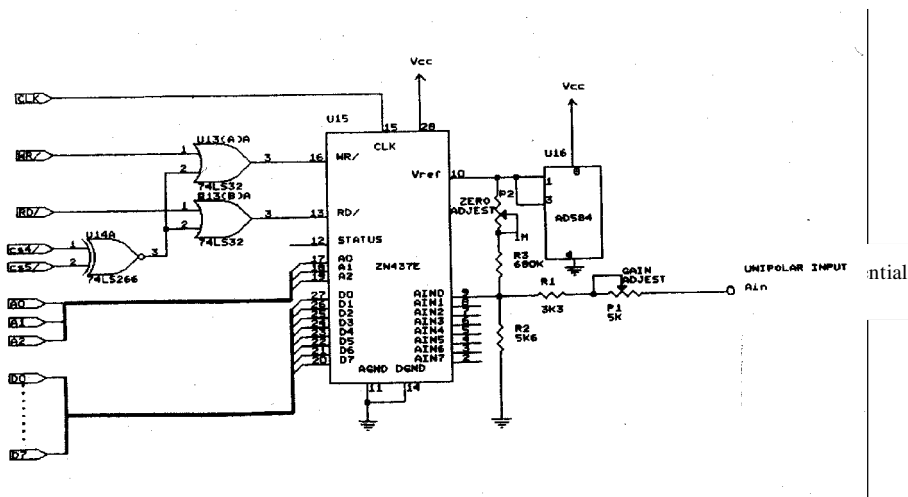


Figure 4. A circuit diagram showing how an 8-channel 8-bit ADC is interfaced on PC's data bus, address bus and control bus for data acquisition from the pH/mV meter for automated potentiometric titration.

The ADC used in this study was ZN437, which is an 8-bit and 8-channel ADC (Figure 4) and easily interfaceable with most popular microprocessors [13]. It consists of an 8-bit successive approximate A-D converter, an 8 channel multiplexer, 8 x 8 bit RAM, clock pre-divider, control logic and double buffered latches with 3-state outputs. ZN437 can be programmed for any one of four possible conversion modes: 1) single shot conversion on a named channel, 2) continuous conversion on a named channel, 3) single shot conversion on all channels, and 4) continuous conversion on all channels. For this work the ADC was configured in mode 2, *i.e.* continuous conversion on named channel.

Automated potentiometric titration of iron(II). Figure 5 shows a scattered titration graph obtained by titration of pure ammonium iron(II) sulphate by potassium dichromate solution using PC automated potentiometric titrator. The lower x-axis of the graph shows the number of data points of potential readings sampled by the drop counter circuitry during automated titration. Each open triangle shows the data points taken by the computer. In the titration curve it can be easily seen that about 86 potential readings were sampled, *i.e.* at each drop for a single titration. The total volume of the potassium dichromate used for this titration was only 4.3 mL. As it can be seen in the curve the readings taken are very close at about 0.05 mL intervals.

Practically it was very difficult for chemists to perform the same titration at every drop interval mainly due to the impossibility to dispense the titrant and to measure the exact volume of the titrant. The upper x-axis (Figure 5) is the titrant volume axis generated by the MicroCal origin software by correlating the total volume consumed for the titration with that of the number of data points acquired by the computer. Since the titration was carried out at every drop of the titrant, the total volume consumed was proportional to the number of data points taken. Therefore, the equivalence point can be easily obtained in the form of volume of titrant from the upper x-axis, which is computer generated volume axis. The first and the second derivative curves could also be easily drawn by just a single mouse click from the MicroCal Origin software menu.

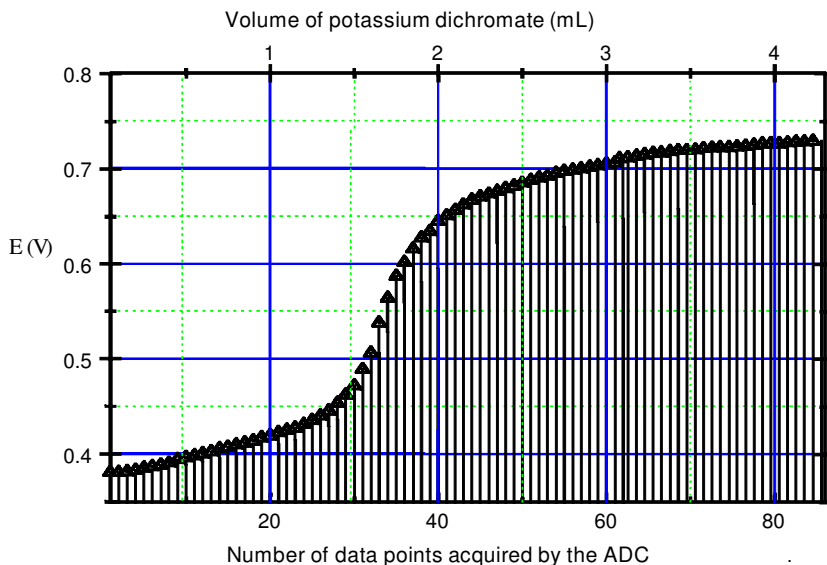


Figure 5. Potentiometric titration curve of 1.50×10^{-4} M ammonium iron(II) sulphate titrated with 8.69×10^{-3} M of potassium dichromate solution. The triangles show the potential readings taken by the computer and the drop lines show the corresponding data point number.

As it can be seen in Figure 5 due to the closeness of the data points the exact shape of the titration curve could be easily obtained without any extrapolation of the graph. This is really a great advantage to exactly see the titration curves specially if the titration has more than one equivalence point.

In this method of titration the use of expensive automatic syringe pumps or digital burettes for automated titration was replaced by the use of normal burette with PC interfaced IR source detector system. The chemist could just start the titration experiment through software and he can do something else during the titration process, he can also pause the titration at any time and resume and stop the titration as he wishes. This has a great advantage especially for laboratories doing many routine titrations every day and for determination of exact titration curves.

Figure 6 shows three important titration graphs drawn in the form of line by the use of MicroCal Origin software. The first titration curve (a) was a plot of electrode potential in volt against number of data points sampled by the ADC (lower axis) and volume of titrant in mL (upper x-axis). The second graph (b) dE/dV is obtained by first derivation of the first titration curve and the third curve (c) is just the second derivative, d^2E/dV^2 where both are obtained easily by the software. The second derivative curve was used for an easy location of the equivalence point and the volume of the titrant used. Since this curve is vertically crossing the volume axis it was very easy to read the equivalence volume of the titrant by just putting the data reader cross over it.

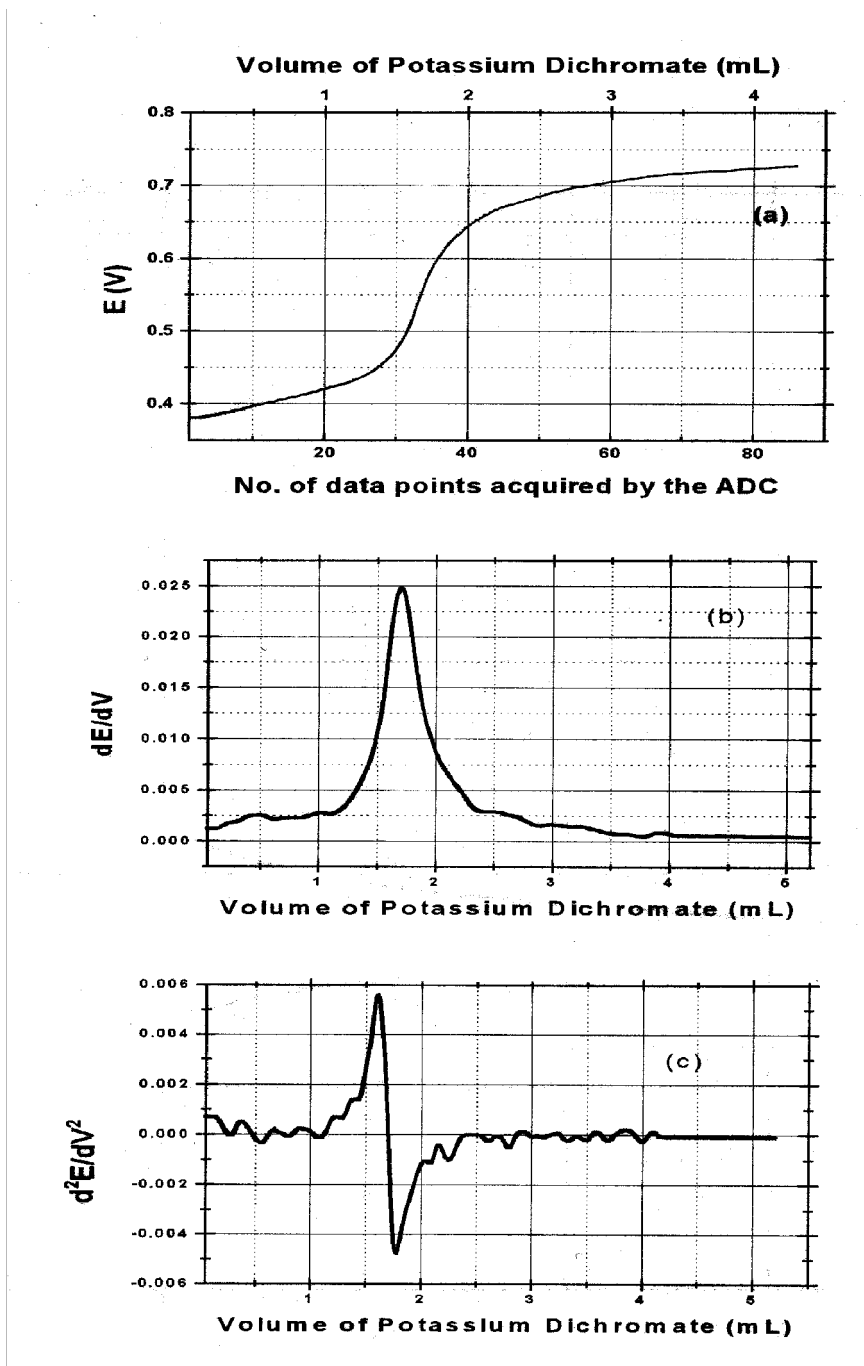


Figure 6. Automated potentiometric titration curves of 0.00015 M ammonium iron(II) sulphate solution titrated with 0.00869 M potassium dichromate solution. Curve (a) is the normal titration curve, curve (b) and (c) are the first and the second derivatives plotted by MicroCal Origin Software.

Table 1. Comparison of experimentally found concentration of iron(II) from PC automated potentiometric titration with that of known values. The standard deviation, percent relative standard deviation and relative errors (found for n = 3) are also indicated.

Sample No.	Concentration of iron(II) (mg/L)		Standard deviation [*]	RSD (%)	Relative error (%)
	Known value	Experimentally found mean value			
1	710	714	7.940	1.12	0.56
2	200	198.9	6.560	1.19	0.55
3	142.8	142.2	2.260	1.58	0.42
4	71.4	71.18	1.240	1.74	0.45
5	35.7	35.47	0.490	1.78	0.65
6	17	17.19	0.167	1.86	1.68
7	8.65	8.50	0.066	2.19	1.76

The percent relative standard deviation (%RSD) was increasing as the concentration of iron(II) to be determined decreases. From Table 1 it can be seen that the %RSD tends to increase from 1.12% for experimentally found mean concentration of 714 mg/L to 2.19% for mean concentration of 8.5 mg/L of iron(II). The overall trend of the percent relative error also tends to increase as the concentration to be measured decreases. From the table it can be easily seen that the percent relative error for the known concentration of 710 mg/L iron(II) was 0.56% where as for the minimum concentration tested which is 8.65 mg/L, the relative error increased to 1.76%. Therefore, with this PC automated potentiometric titration method it was possible to measure iron(II) concentration down to 0.00015M with percent relative error of less than 2%, which is quite better than manual potentiometric titration and titrations that use indicators.

Advantages and applications of PC automated potentiometric titration. The PC automated potentiometric titration have many advantages which includes: 1) acquisition of large amount of data in a short period of time, 2) avoids human errors that are common during manual titration, 3) it frees the experimenter from tedious iterative tasks and allowing him or her to dedicate more attention to experimental design and interpretation of data, 4) it increases the experimental precision and accuracy, and 5) the experimental data can be stored in a computer memory and then can be analyzed, printed and plotted with any graphics software. In this study the system designed was tested only for automation of titrimetric analysis of iron(II), but it can also be used to automate many other forms of titration such as: neutralization reaction titrations, acid-base titrations in aqueous medium, acid-base titrations in non-aqueous medium, precipitation titrations and complex formation titrations [14]. There are very large number of processes on which PC automated potentiometer is applied. In many continuous processes, the automated potentiometer is used for monitoring the amounts of ionic species present in solution under process. Furthermore automated potentiometric titrators are used to analyze billions of samples annually in clinical chemistry and biochemistry laboratories. Some of the possible applications of the PC automated potentiometric titrations include the determination of: sodium thiosulphate or of iodine by titrating it with potassium permanganate, chlorine with standard sodium thiosulphate, copper with standard sodium thiosulphate, chromium with standard solution of ferrous ammonium sulphate, manganese(II) with permanganate ion in neutral pyrophosphate solution, sulphate with standard lead nitrate solution in the presence of a ferrocyanide-ferrocyanide redox system., ferric ion with standard EDTA solution, and aromatic amines and sulphanyl amides with standard sodium nitrate solution.

REFERENCES

1. Dessy, R.E. *Ed. Anal. Chem.* **1985**, 57, 77.
2. Dessy, R.E. *Ed. Anal. Chem.* **1985**, 57, 310.
3. Kay, A. *Sci. Am.* **1984**, 251, 52.
4. Cerda, V.; Ramis, G. *An Introduction to Laboratory Automation*, John Wiley: New York; **1990**; p 256.
5. Liscouski, J.G. *Instrumentation in Analytical Chemistry* **1982**, 86, 97.
6. Tolpey, M. *PC-Based Instrumentation and Control*, Clays Ltd.: Great Britain; **1995**; 6, 7.
7. Bassett, J.; Denney, R.C.; Jeffery, G.H.; Mendham, J. *Text Book of Quantitative Inorganic Analysis*, Longman: New York; **1978**.
8. MicroCal Software Inc, *Technical Graphics and Data Analysis in Windows*, Northampton: USA; **1995**.
9. Eggebrecht, L.C. *Interfacing to the IBM Personal Computer*, Howard W. Sams & Co. Inc: Indiana, USA; **1989**; pp 142,145.
10. Desta, M. *Interfacing Instruments to Personal Computers*, Project Paper, International Atomic Energy Agency's Seibersdorf Laboratories: Austria; **1990**; pp 13, 17, 20.
11. Intel, *Programmable Interval Timer data sheet*, Intel Corporation: USA; **1985**; p 40.
12. Intel, *Programmable Peripheral Interface data sheet*, Intel Corporation: USA; **1985**; p 122.
13. GEC Plessery, *Zn 437E an 8-bit and 8 Channel Analog to Digital Converter Data Sheet*, GEC Plessery Semiconductors: USA; **1989**; pp 1, 2.
14. Skoog, D.A.; West, D.M. *Principles of Instrumental Analysis*, Holt, Rinehart and Winston, Inc.: New York; **1971**; p 181.