

An automatic system for potentiometric titrations

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Summary - An automatic acquisition and processing system for titration data based on a PC-compatible is described. The main advantages over the commercial available units are the possibility of using an uniform and objective criterion of potential stability, greater flexibility and much lower price. The titration system and its interfacing to the microcomputer is described as well as the controlling software written in GWBASIC. Examples of potentiometric acid-base titrations using the proposed system are discussed.

Introduction

Since their introduction, PC computers have found widespread use for instrument control and the acquisition and analysis of data. Due to their low cost and improved performance, they are recognised as an economical way to develop automated systems, or to overcome the restrictions associated to the instrumentation commercially available.

In the course of our work we faced the problem of determining reliable acid-base or complexometric equilibrium constants of humic matter. For the obtainment of good results an automatic system must be used. However, the brand name titration systems are either very expensive and/or do not meet the demands of flexibility, accuracy and reliability necessary for our research needs. Therefore, we decided to assemble our own system based in microcomputer, pH meter and automatic burettes.

Experimental

Experimental techniques

The titration cell was fitted with a plastic lid with inlets for the electrodes, thermometer, N₂ gas and burette tip. The N₂ gas used to ensure a CO₂-free atmosphere over the solution was bubbled through NaOH 15% and KNO₃ 0.1 M solution. Carbonate free 0.1M NaOH solutions were prepared by dilution of NaOH 50%. The necessary volume of the concentrated solution was measured with a plastic syringe and filtered through a Dyna Gard 0.2 μm syringe filter, into a polyethylene bottle containing cold pre-boiled water, under nitrogen. The polyethylene bottle was connected to the automatic burette and fitted with a soda-lime guard-tube. Solutions of HCl were prepared from concentrated HCl and standardised against sodium tetraborate. Acid solutions were prepared in the cell, by mixing known volumes of HCl standard solution and/or a known weight of potassium hydrogen phthalate with KNO₃ solution in order to adjust the ionic strength to 0.1 mol dm⁻³.

An ORION ROSS 8172 combination electrode was used. Prior to the titrations the electrode was calibrated with home-made buffers with an ionic strength adjusted to the same value of the solutions to be titrated [1].

The titrations were performed under high quality nitrogen, and the double-walled titration cell was kept at 25 ± 0.1°C, by circulation of thermostated water.

All reagents were A.C.S. grade.

Hardware

Figure 1 illustrates the general arrangement of the equipment used for the experiments.

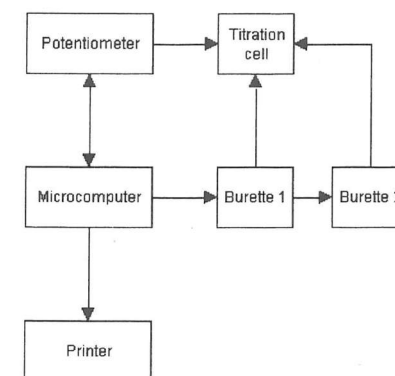


Figure 1 - Schematic diagram of the hardware arrangement

The microcomputer was a PC-compatible, based on a 80386, 25 MHz CPU with 4M of RAM and fitted with two RS-232 serial ports. One serial port is used for the communication to the potentiometer and the other to control the automatic burettes.

The potentiometer was a CRISON micropH 2002, with a resolution of 0.001 pH units or 0.1 mV.

The burettes were two CRISON microBur 2030 with interchangeable Hamilton syringes and able to deliver volumes in steps of 1/2500 of the total syringe volume. Both burettes communicate with the PC through the same serial port (Baud rate=2400, even parity, 7 Bits, 2 Stop Bits).

Data communication between the microcomputer and the potentiometer is in ASCII format and transmitted via a RS-232 connection (Baud rate=1200, No parity, 8 Bits, 2 Stop Bits).

Software

Figure 2 shows a flowchart of the major details of the program TITED used for data acquisition.

The program was written in GWBASIC and it performs three main tasks: titration, calibration and burette washings. The first two tasks call for a subroutine

(READPH), that gets the data from the potentiometer and checks if the stability criterion previously defined has been attained.

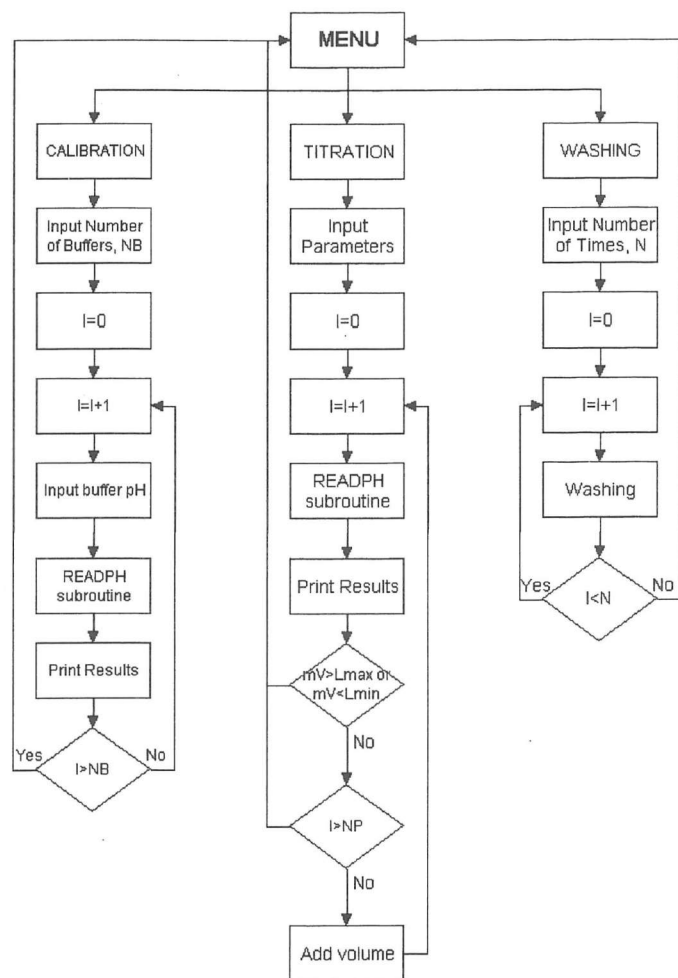


Figure 2 - Flowchart of the program TITED used for data acquisition

Figure 3 outlines the flowchart of the subroutine READPH. The algorithm used to define the stability criterion is based on the following parameters:

- number of readings (NR)
- acceptable drift (DRIFT)
- minimum time to stay stable (TSTAB)

- maximum time to wait for the stability criterion to be attained (TMAX).

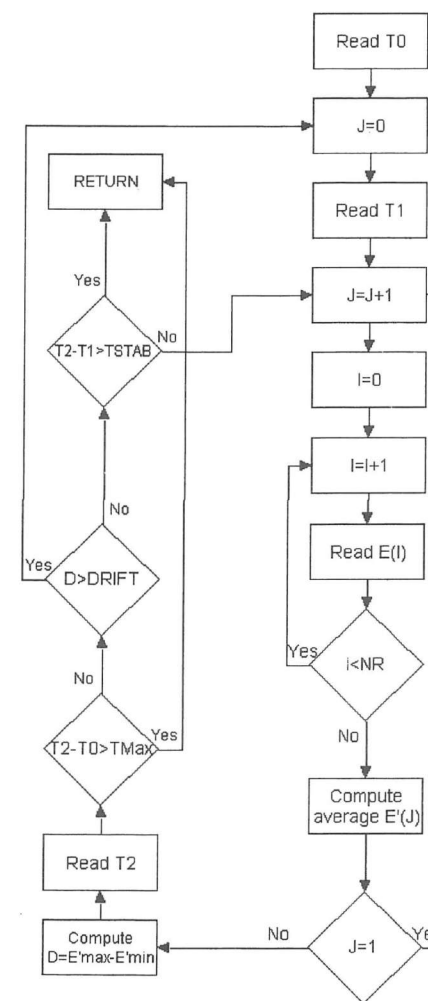


Figure 3 - Flowchart of the subroutine READPH

When this subroutine is called, a clock is triggered and it starts reading of the potential values every three seconds. The averaged values of each NR readings are calculated sequentially, the maximum and minimum of these averages being retained. The stability criterion is met if the difference between these two extremes is less than the drift for a time interval longer than TSTAB and shorter than TMAX.

The titration module starts with the input of the following parameters:

- the ones needed for the stability criterion previously mentioned
- burette volume (VT)
- volume increments of titrant to be added in each titration point (AD)
- number of titration points (NP)
- potential end value (Lmax or Lmin)

The criterion to end the titration is based either on the number of titration points or on the potential value. After each titrant addition, the subroutine READPH is called. When the stability criterion is attained, the last average value of the potential and the corresponding titrant volume are saved in ASCII format, and then a new volume increment is added.

For the calibration module the program obtains only the potential values for each standard according to the stability criterion defined for this task. The values of the pH and potential for the standards are saved in an ASCII file for further processing.

Validation of the system

As a test for this automatic system, titrations of a strong and a weak acid with sodium hydroxide were performed. The results of each titration, potential versus titrant volume, saved in an ASCII file, were imported to the spreadsheet of SigmaPlot program [2], in order to make the necessary calculations and graphics.

The results from hydrochloric acid titrations with sodium hydroxide were analysed by the Gran method [3]. As an example, the Gran plot for one of those titrations is presented in Figure 4. Gran equations for the two branches of the Gran plot are presented in Table 1.

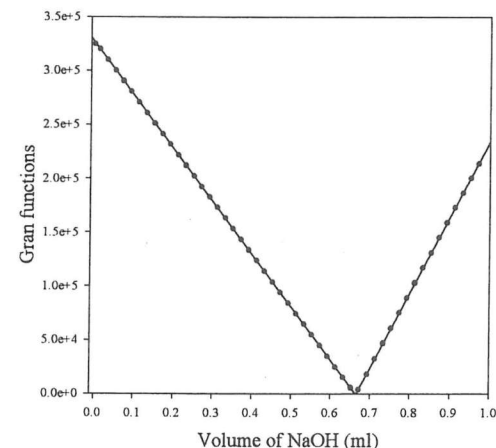


Figure 4 - Gran plot for one of the titrations of HCl with NaOH

Table 1 - Gran equations for the titration of HCl with NaOH

	Gran equation
	V_0 =initial volume in the cell; V_B =added volume of base; E =potential reading; K_w =ionic product of water; E^0 and s are the calibration parameters ($E=E^0-s$ pH)
Before equivalence	$(V_0 + V_B)10^{E/s} = C_B 10^{E^0/s} (V_e - V_B)$
After equivalence	$(V_0 + V_B)10^{-E/s} = \frac{C_B}{K_w 10^{E^0/s}} (V_B - V_e)$

Six titrations were performed. Correlation coefficients higher than 0.999 were always obtained for the two straight lines of the Gran plot, adjusted to the experimental results by the least-squares method. The values for the equivalence volume obtained from the intersection of each of the two branches of the Gran plot with titrant volume axis, did not differ more than 1.5% of their mean value. That coincidence and the linearity of the two branches put into evidence the absence of carbonate in the sodium hydroxide solutions.

The ionic product of water, K_w , was calculated from the slope of the Gran plot branch corresponding to points after the equivalence ($\text{pH} > 7$). The average of the K_w values calculated from each titration is presented in Table 2, together with literature values [4,5] obtained in the same conditions of temperature and ionic strength.

For the analysis of the results from phthalic acid titrations, phthalic acid was modelled as a mixture of two monoprotic acids of equal concentration and the corresponding Simms constants [6] were determined by non-linear regression analysis of the data. The CurveFit facility of SigmaPlot program was used. The acidity constants of phthalic acid, calculated from the Simms constants, are presented in Table 2 and show good agreement with the reported literature values [7,8].

Table 2 - Ionisation constants of phthalic acid and ionic product of water at 25°C and ionic strength 0.1 M

		This work		Literature values	
Phthalic acid	$\text{p}K_1$	2.748	(0.004) ^a	2.75 ± 0.02 [6]	2.76 ± 0.03 [7]
	$\text{p}K_2$	4.921	(0.002) ^a	4.93 ± 0.01 [6]	4.92 ± 0.05 [7]
Water	$\text{p}K_w$	13.778	(0.018) ^a	13.778 [3]	13.78 ± 0.01 [7]

^a standard deviation

Conclusions

An automatic acquisition and processing system is proposed for achieving time consuming potentiometric titrations without operator intervention. Flexibility and much lower price are the main advantages of the proposed system relatively to the commercial available units.

The proposed system allows the definition of an adequate, uniform and objective stability criterion for potential readings, in each titration. The data, potential versus titrant volume, are saved in an ASCII file, from which they are easily imported to other programs in order to make the necessary calculations and graphics.

The ionic product of water and the ionisation constants of phthalic acid determined using the proposed system are in good agreement with literature values, obtained at the same temperature and ionic strength.

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