An Automatic Differential Potentiometric Estimation Technique

M.JAFFAR AND S.NOORULLAH HUSAINI
Department of Chemistry,
Quaid-i-Azam University,Islamabad, Pakistan

Summary:A new differential potentiometric technique based on a simple, inexpensive RC filter circuit, capable of producing primary derivative signals, is presented for quantitative differential potentiometric work. The relevant experimental set-up to carry out automatic potentiometric titrations is designed and its performance is demonstrated for various weak/strong acid-base combinations. The technique has the potential of application to other areas of potentiometric estimation such as compleximetry and redox titrimetry. The overall average accuracy of the method when applied to a set of 16 acid-base combinations turns out to be about 1.5% with a precision of ± 1% in duplicate runs.

Introduction

Over the past several years advances in the field of electronics have provided new shape and refinement to most of the chemical instruments used frequently in laboratories. These advances include basis modification in circuit design, introduction of a new operational flexibilities and incorporation of automatic functioning characteristics. Consequently both reliability and precision attainable in instrumental analyses have gone up in almost every branch of analytical work without exception. The field of electrochemistry, in particular, has witnessed the introduction of many such positive innovations during the past two decades, easpecially in todays most advanced area of potentiometric estimations where, to begin with a, a humble semiautomatic burette was introduced [1,2] towards automation. An impulse method was presented later by Oehme [3] to deliver microliters of a given liquid with an accuracy of about ±

5%. These attempts were made to augment an automatic potentiometric titration apparatus developed in early 1948, employing a motor driven syringe for delivering known volume of liquids [4]. Subsequently, Haslamb and Squirrell [5] and Irving and Pettit [6] introduced similar systems with minor modifications and improvements to carry out the potentiometric work on an automatic level. In 1963, a differential amplifier was used for the first time for the detection of the end point of a titration by Narayanan and Sundararajan [7]. Miyake [8] described an automatic titrator for conventional applications with the titrant added intermittently; the titration curve recorded had a stepwise configuration thus having an inherent susceptibility to computational errors.

The technique presented here is based upon the production of a new electronic RC filter circuit capable of

yielding analytical results of high accuracy and precision in addition to having the obvious advantages of very low cost and ease of operation over the earlier conventional and complicated differentiator circuits. In conjunction with the proposed experimental set-up for carrying out fully automatic potentiometric estimation, the simple RC circuit described can be used in various automated modes for precise quantitative work in potentiometry.

Circuit Design and Method

The RC circuit design is shown in Figure 1-a where the fixed component values have been indicated. When coupled to the auxiliary circuitry given in Figure 1-b, the RC circuit acts as a high-pass filter having a unique phase-inverting ability. Since during a potentiometric titration the millivolts on a pH meter scale change from a known finite value through zero to another finite value, the trapping of the equivalence point corresponding to zero mv by means of RC circuit becomes easily accessible since at this point the circuit capacitance inverts the mv pulse instantaneously. However, in order to record this inversion point the out-put impulse voltage has to be kept at a reasonably
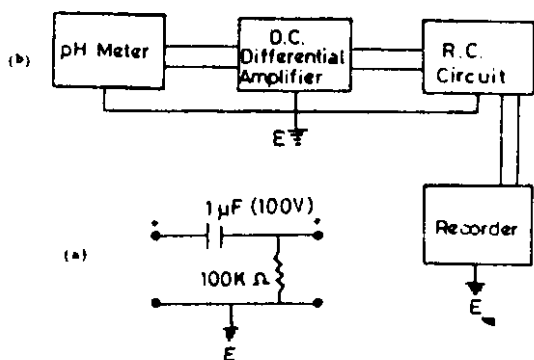
detectable limit. This can be accomplished by incorporating a differential amplifier in the circuit before the signal is fed for recording; Figure-2 gives a self explanatory version of the experimental set-up to carry out automatic potentiometric tirations.

A Kent pH meter, model 7020, with feasibility for electrical out-put outlet, in conjunction with a conventional combination electrode system, was used. The DC differential amplifier used was Accudata (Honeywell, Series 122) at a fixed gain fo 1 x 50. Any other simple D.C. differential amplifier with a similar gain value may be used instead. A multispeed potentiometric recorder, Servogor 310, was used for recording the differential curves.

Before starting an automatic titration, the pH meter was given a 15-20 min warm-up time, and was then calibrated with buffer solutions of known

Fig.1: Electronic Circuit for Automatic Differential Potentiometric Titrations:
(a) High-phase inverter (RC)
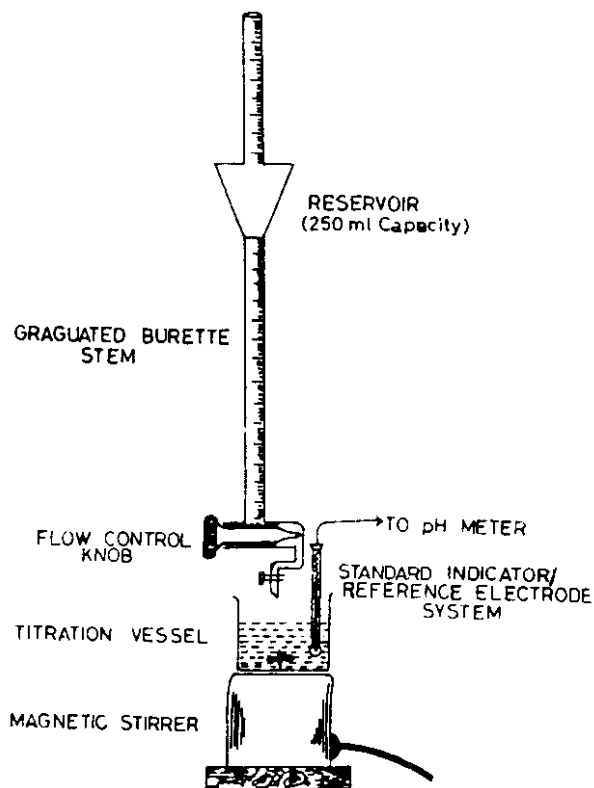(b) Auxiliary Circuit

Fig.2: Schematic Autotitration Set-up

pH through the usual procedure. After calibration, the electrode system was immersed in the titration vessel containing 70.0 ml of the unknown acid or base sample made up from 20.0 ml aliquot diluted with distilled water. The flow rate of the titrant was determined using the upper graduated burette stem serving as indicator of liquid flow that can be controlled through the flow adjusting knob with the burette tap in fully open position. An electric time clock or a stop-watch can be used for flow rate (ml/min) measurement. The reservoir shown is an inverted conical flask (Pyrex, 250 ml) fused in between the two stems of a graduated burette; it permits high constancy of delivered volume upto 100 ml. The average % error encountered in maintaining constant flow rates was estimated at 0.5% for duplicate runs. Normally a flow rate of 15-20 ml/min was found adequate for practical purposes. The differential automatic plot recorded by using the set-up appears in Figure 3-a where the peak maximum corresponds to zero mv (pH = 7). For comparison purpose an unintegrated version of the plot as a sigmoid curve appears in Figure 3-b. It is obvious that from the time scale along the X-axis of the chart paper, the volume of titrant used, at equivalence point against unknown concentration of the acid or base can be determined. Other RC combinations with low capacitance time (< 0.1 sec)

Figure 3.: (a) A typical differential curve (b) An undifferentiated sigmoid curve

have also been found suitable for obtaining sharp differential curves.

Results and Discussion

In Table 1 are listed the actual and estimated quantitative results for a varied variety of acids and bases selected for automatic potentiometric titration purpose. The actual values were obtained through direct potentiometric titration procedure with equvalance point at pH 7. The selection of the acid-base combinations was rather tentative because the main objective of the present investigation was to check, in the first place, the applicability of the proposed technique on such acid-base systems which differ widely in respect of their dissociation constants. This consideration has important bearing in potentiometric estimations carried out manually since in the case of conventional sigmoid potentiometric curves, the precision with which the equvalance point is located on a curve depends upon the distribution of tagential slope (along the curve) as a function of rapidly changing electrode potential. In other words, only strong acid-base combinations are the ideal ones since a balanced potential drop, or increase, is observed for species dissociated to an equal extent. Consequently, any difference in the dissociation constants of the two species results in the production of a sigmoid curve with uneven slope distribution where from it is practically impossible to pin-point the exact equvalence point, and hence to extract quantitative information. On the other hand, it may be seen from the quoted values of concentrations based on the present differential technique, that the method proposed is independent of the nature of the acid-base combination taken for estimation. For both strong/weak, strong/strong, and weak/weak acid-base systems it applies equally well, and successfully covers a concentration range of $1-10^{-5}M$.
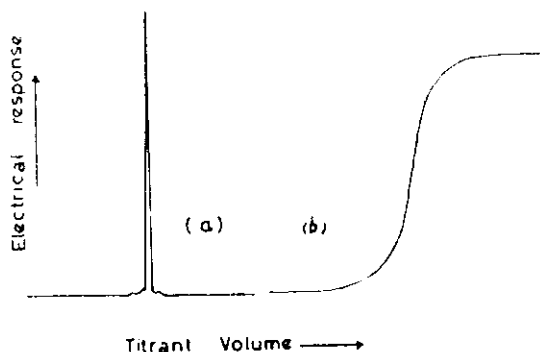
Table-1: Actual vs. estimated concentrations of various
acid-base systems

System	Actual Concentration N (eq./lit) $\times 10^2$	Estimated Concentration N (eq./lit) $\times 10^2$	Error (%)
$NaOH - (COOH)_2$	1.90	1.87	1.57
$NH_4OH - (COOH)_2$	1.46	1.43	2.05
$H_2SO_4 - NaOH$	1.81	1.78	1.65
$HNO_3 - NaOH$	1.80	1.78	1.11
$HCl - NaOH$	1.76	1.73	1.70
$(CH_2COOH)_2 - NaOH$	1.69	1.67	1.18
$CH_2(COOH)_2 - NaOH$	2.25	2.23	0.88
$CH_3(COOH) - NaOH$	2.30	2.27	1.30
$ClCH_2(COOH) - NaOH$	1.78	1.76	1.12
$H_2SO_4 - NH_4OH$	1.81	1.79	1.10
$HNO_3 - NH_4OH$	1.80	1.85	2.77
$HCl - NH_4OH$	1.76	1.73	1.70
$(CH_2COOH)_2 - NH_4OH$	1.69	1.73	2.36
$(CH_2COOH)_2 - NH_4OH$	2.25	2.26	0.44
$CH_3(COOH) - NH_4OH$	2.30	2.28	0.87
$ClCH_2(COOH) - NH_4OH$	1.78	1.74	2.20

For all 16 combinations listed, a maximum deviation of ± 0.0004 N was observed between the actual and computed values· of concentrations. This corresponds to an average error of about ± 1.5%. A precision of ± 1% for a given system in triplicate measurements has been established. However, the overall accuracy of the method depends on the accuracy of flow measurement which has been found not to very beyond ± 0.5% for volumes of the titrant delivered as high as 100 ml. The technique has the potential of application to other types of potentiometric estimations such as compleximetry and redox titrimetry.

References

1. S.Gordon and C.Campbell,
   Anal.Chem. **29**, *1706, (1957)*
2. J.Farquharson,
   Rev.Sci.Instr., **31**, *723, (1960)*
3. F.Oehme,
   Z.Anal.Chem. **222**, *244, (1966)*
4. J.J.Lingane,
   Anal.Chem., **20**, *285, (1948)*
5. J.Haslam and D.C.M.Squirrell,
   J.Appl.Chem.(London), **9**, *65,(1959)*
6. H.Irving and L.D.Pettit,
   Analyst, **84**, *641, (1959)*
7. U H.Narayanan and K.Sundararajan,
   J.Electroanal.Chem., **6**, *397, (1963)*
8. S.Miyake,
   Talanta, **13**, *1253 (1966).*