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RESEARCH ARTICLE

On-line Determination of Hydrochloric Acid in Process Effluent Streams by Potentiometric Sequential Injection Acid-Base Titration

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Abstract

An on-line potentiometric sequential injection acid-base system for the titration of a hydrochloric acid solution with a standard sodium hydroxide solution in process effluent streams is proposed. A solution of 0.1 mol/l sodium chloride is used as carrier. The sample is sandwiched between two titrants in a holding coil, with the volume of the first base being twice to that of the second one and channeled by flow reversal through a reaction coil to the potentiometric sensor. A linear relationship between peak width and logarithm of the hydrochloric acid concentration was obtained in the range 0.025 mol/l - 0.05 mol/l of hydrochloric acid when a solution of 0.001 mol/l sodium hydroxide was used for the titration. Samples from process effluent streams were used to evaluate the feasibility of the method with that of an automated and manual titration. The results showed good agreement between the different methods. The percentage relative standard deviation (RSD %) was found to be less than 0.22. The sample frequency is 30 samples per hour.

Keywords Potentiometric sequential injection acid-base titration, hydrochloric acid, process effluent streams.

1. Introduction

Titration is one of the most common and widely used analytical methods. It is very reliable, easily understood and readily applicable as analytical tool in process analysis. The main drawback of titrimetric procedures are the time consumption and labour intensive operations as well as the troublesome processes of collecting and plotting the data for the titration curve. This stimulated research in the automation of titrimetric procedures. Automatic titration can be classified into automated titrations using an automatic burette or flow titrations (flow injection and sequential injection titrations). The main disadvantage of many automated burette titration systems is that they are still based on batch operations and therefore require complicated ancillary units to facilitate sample introduction, draining and washing of the titration vessel, and usually replenishing the titrant in the delivery unit. De Caro[1] described an automated titrator based on the use of a sample changer with two towers. During a sample series, the subsequent samples are mixed or diluted at one tower, while the actual samples are analyzed at the other tower. The author claimed that time is saved and productivity is increased. Although the system shows a vast improvement, the automated titrator is still based on a batch operation and together with many of these developed automated titrators still suffered from the disadvantages mentioned above.

Many of these problems are overcome by using flow injection analysis (FIA). In 1977 Ruzicka *et al*[2] developed a flow injection titration method based on gradient exploitation where the distance between two points of identical amplitude in an analytical signal is proportional to the logarithm of the concentration. They made use of a gradient chamber where the sample and the titrant were mixed and a chemical reaction occurred. The titrant was used as a carrier. Since then several flow injection titration systems have been proposed and developed[3-20] and some have been implemented in process monitoring. One of the big disadvantages of these methods is the high reagent (titrant) consumption. The introduction of sequential injection titration in 1997[21] overcame this drawback by replacing the continuous flowing titrant stream of the flow injection titration system with two titrant zones on either side of the sample zone in a distilled water carrier stream. The system was expanded to the determination of sulphuric acid in process effluent streams from a copper plating industry[22]. Both these systems however still used colour indicators.

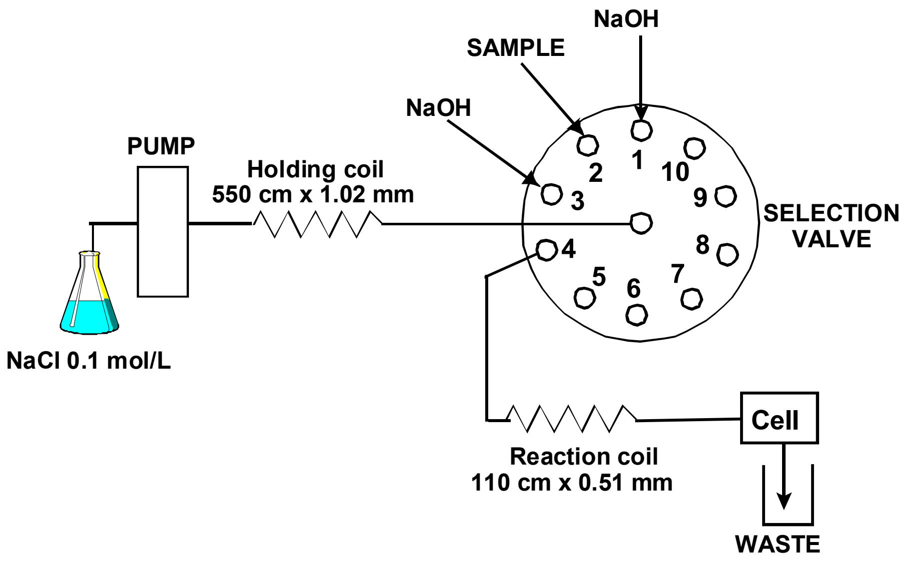
Our laboratory was approached to develop an analyser capable of monitoring the hydrochloric acid concentration in the process effluent streams of a hydrochloric acid production plant for environmental purposes. One of the prerequisites of the analyser was that the system should be simple and robust, reliable with a low frequency of maintenance and that the consumption of reagents should be very low and economically utilised. Further prerequisites were that the analyser should be able to determine the hydrochloric acid concentration accurately between 0.03 and 0.05 mol/l and that it should be able to screen higher acid concentrations with an alarm system in order to warn the production plant that the environmental limit has been exceeded. SIA seemed to be an ideal detector for such an analyser and this paper reports on a system that was developed for this purpose. The colour indicators previously[21,22] used were replaced by a pH electrode sensor.

The concept is based on the aspiration of the acid sample between two base zones with the first base zone two times that of the second base zone. The dispersed sample zone becomes gradually neutralized by the base penetrating through the interfaces. At the front and the tail of the sample zone an element of fluid exists within which the acid is exactly neutralized by the base[21,22]. The two equivalence points form a pair, having the same dispersion, and their physical distance will increase with increasing concentration of the injected sample.

2. Experimental

2.1. Apparatus

The basic sequential injection system (SIA) is illustrated in Fig. 1. It was constructed from a Gilson Minipuls 3 peristaltic pump (Villiers-le-Bel, France), a 10-port electrically actuated selection valve (Model ECSD10P, Valco Instruments, Houston, Texas, USA), and a pH electrode (Hamilton, Switzerland) connected to an Orion Research Microprocessor Ionalyzer (Model 901). Data acquisition and device control were achieved using a PC 30-B interface board (Eagle Electric, Cape Town, South Africa) and an assembled distribution board (MINTEK, Randburg, South Africa). The flowTEK[23] software package (obtainable from MINTEK) for computer-aided flow analysis was used throughout for device control and data acquisition. Tygon tubing was used for the construction of the holding (HC) and the reaction coils (RC). The length and diameter of the tubing used are indicated in Fig. 1.



A. SCHEMATIC FLOW DIAGRAM

B. DEVICE SEQUENCE FOR ONE SIA CYCLE

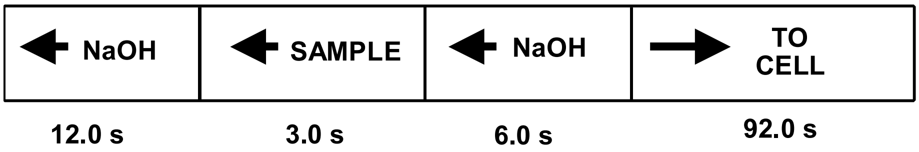


Figure 1 (A). Schematic representation of sequential injection titration system.
(B). Device sequence for one cycle of the sequential titration system.

The results obtained with the proposed system were compared with the results obtained from an automated batch titration system as well as manual titration. An automatic burette (Metrohm Dosimat 665) for automated titration and an ordinary burette for manual titration were used.

2.2. Reagents and Solutions

All solutions were prepared with chemicals of analytical grade. De-ionized water from a Modulab system (Continental Water Systems, San Antonio, TX, USA) was used to prepare all solutions and dilutions.

Sodium Chloride Solution

A 0.1 mol/l sodium chloride solution was used as a carrier stream. The solution was obtained by dissolving 11.688 g of dried sodium chloride in 2 l de-ionized water.

Sodium Hydroxide Solutions

Sodium hydroxide working solutions were prepared by appropriate dilution of 0.1001 mol/l sodium hydroxide stock solution (Titrisol standard solution, Merck), standardized against potassium hydrogen phthalate (Merck).

Hydrochloric Acid Standard Solutions

Standard hydrochloric acid solutions in the range 0.025 - 0.05 mol/l were prepared by appropriate dilution of a stock 0.917 mol/l hydrochloric acid solution standardized against the 0.1001 mol/l sodium hydroxide solution.

Samples

Effluent samples downstream from a hydrochloric acid production plant were obtained and directly analysed on the system without any sample pretreatment.

2.3. Procedure

Table 1 shows the basic device sequence to complete one cycle. The titration carried out involved first the aspiration of a base zone for 12.0 s, then an acid sample zone for 3.0 s and finally the second base zone for 6.0 s into the holding coil as depicted in Fig. 1B. The stack of zones in the holding coil were swept by flow reversal via the reaction coil through the pH electrode as sensor. The time needed to complete one cycle was 120.0 s and the pump returned to its starting position and ready for the next cycle. The sample frequency is of 30 samples per hour. The peak width was measured at a relative peak height of 1600. In the more advanced system port 10 of the selection valve was used as detector line and port 9 of the selection valve as the line for the second sodium hydroxide stream. Valve positions 2-8 were used either for the selection of different hydrochloric acid standard solutions or for different sampling points making the system ideally suitable for automation, quality control and on-site monitoring. The computer was then programmed for the following device sequence: (i) Valve position 1 for the first NaOH solution, valve position 2 for the standard or sample line and valve position 9 for the second NaOH solution aspirated into the holding coil and then valve position 10 for flow reversal of the stack of zones through the reaction coil to the sensor for measurement. (ii) The same device sequence was then followed where valve position 2 in a series of runs were replaced for the different runs by valve positions 3 to 8 for the different sampling points or standard solutions as required. One up to 3 standard hydrochloric acid solutions were aspirated in between the different samples in order to assure quality control of the system.

Table 1 Device sequence for one cycle of the sequential titration system.

Time (s)	Pump	Valve	Description
0	Off	NaOH	Pump off, select NaOH solution (valve position 1)
1	Reverse		Draw up NaOH solution
13	Off		Pump stop
14		Sample	Select HCl sample stream (valve position 2)
15	Reverse		Draw up HCl sample
18	Off		Pump stop
19		NaOH	Select NaOH stream (valve position 3)
20	Reverse		Draw up NaOH solution
26	Off		Pump stop
27		Detector	Pump select detector line (valve position 4)
28	Forward		Pump stack zones to the detector
120	Off	Home	Pump off, return valve to position 1

3. Results and Discussion

The basic theory and concept was originally defined by Ruzicka *et al*[2] in 1977 for flow injection analysis and adapted previously[21,22] for sequential injection analysis using UV/Vis spectrophotometry. This was replaced in the current study by an on-line sequential injection potentiometric titration system to fulfill the requirements in process effluent streams of a hydrochloric acid production plant.

The different titrant and titrand volumes were aspirated into a holding coil whereafter the well defined stack of zones were channelled through a reaction coil to a electrochemical cell for detection. A carrier stream of 0.1 mol/l sodium chloride solution was used. The two base zones and acid zone penetrated and gradually neutralized each other on the boundaries when the flow of the carrier stream was reversed and the zones were propelled to the detector. An element of fluid therefore existed at both the front and tail of the dispersed acid sample zone within which the acid was exactly neutralized by the base. The theoretical concepts behind this were discussed previously[21,22].

3.1. Optimization

There are numerous factors that will influence the peak width of the injected acid sample. The different parameters were varied univariately to obtain an optimum. Optimization of one parameter lead to the other.

Flow Rate

An acid concentration ranging between 0.01 and 0.1 mol/l was titrated in order to study the carrier stream flow rate. The influence of flow rate on relative peak width and % RSD for an acid concentration of 0.03 mol/l is given in Fig. 2.

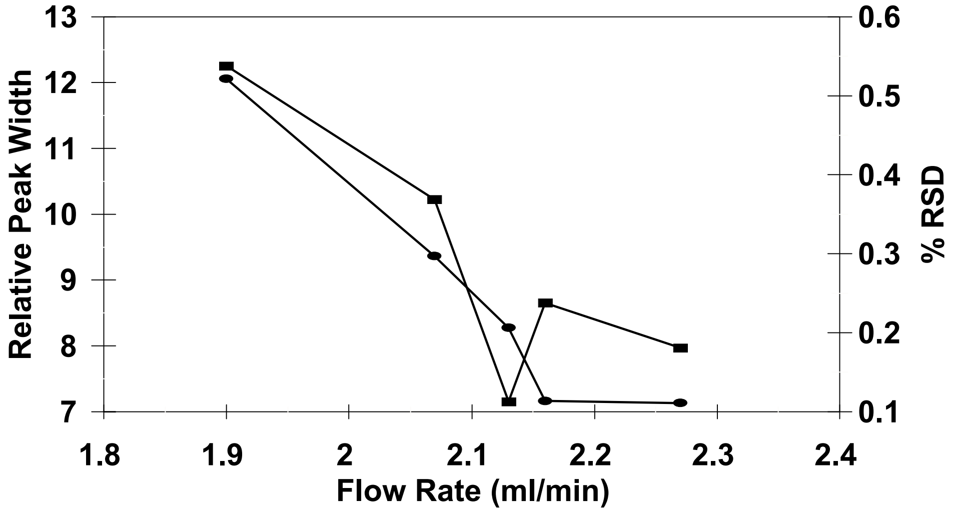


Figure 2 Influence of the carrier stream flow rate on peak width and % RSD. (Circle = Peak width; Square = % RSD).

Although a better sensitivity could be obtained at lower flow rates, 2.13 ml/ min was chosen as optimum because a higher sample frequency was obtained. The SIA system with potentiometric detection confirmed the hydrodynamic flow rate conditions obtained previously with spectrophotometric detection[21,22]. The results furthermore revealed that the relative peak width of the recorded peaks decreased with an increase in flow rate as outlined in Fig 3. This is in accordance with the theoretical principles given previously[21,22] which shows that the slopes of the calibration curves decreased with increasing flow rate.

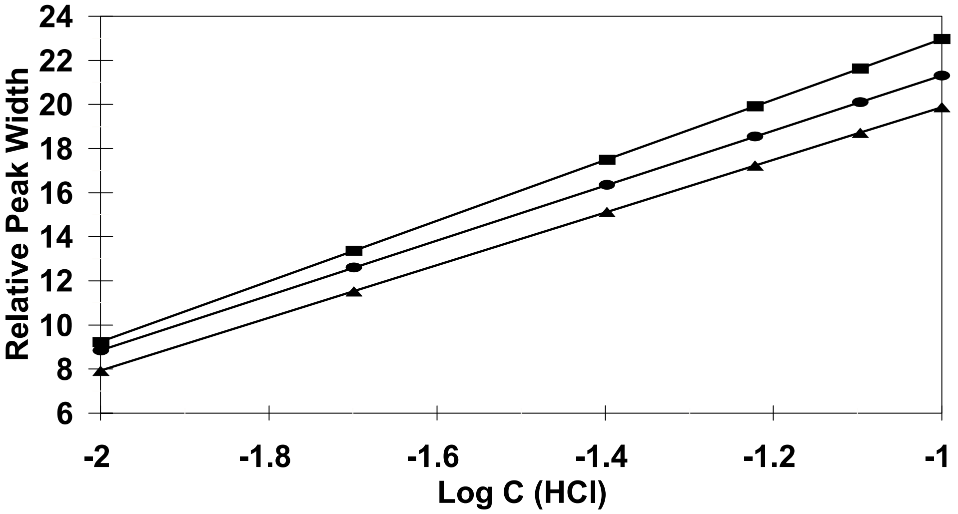


Figure 3 Calibration curves at different carrier stream flow rates. (Square = 1.9 ml/min; Circle = 2.07 ml/min and Triangle = 2.13 ml/min).

The base zone and acid zone volumes were previously[21,22] evaluated, and the results obtained with the potentiometric SIA system show that the volume of the first base zone should be twice that of the second base zone which confirmed previous results.

Sodium Hydroxide Concentration

The resulting relative peak width decreased with an increase in the concentration of the base as illustrated in Fig 4.

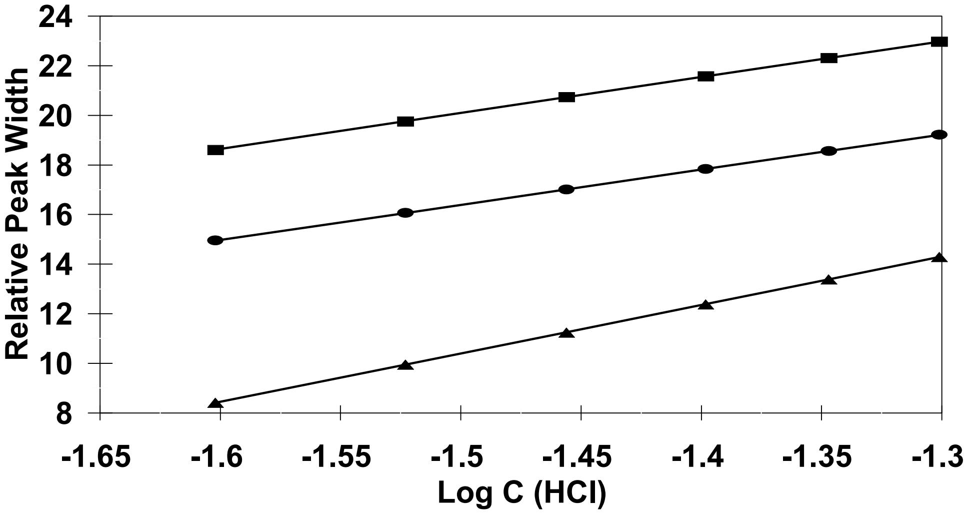


Figure 4 Influence of base concentration on peak width and linearity. (Square = 0.0005 mol/l; Circle = 0.001 mol/l and Triangle = 0.005 mol/l NaOH)

The linear range was also affected by the base concentration. A concentration of 0.001 mol/l NaOH solution was chosen to for the proposed method.

3.2. Method Evaluation

The optimized SI titration system was evaluated with regard to linearity, accuracy, precision and sample frequency. The optimized conditions and a sodium hydroxide concentration of 0.001 mol/ l was used in the evaluation.

Linearity

The SI titration peaks for different acid concentrations are shown in Fig. 5. The dotted line indicates the height at which the peak width of the peaks was measured. The calibration curve for the SI titration system is linear in the range 0.025 to 0.05 mol/l with r^2 = 0.9988 and the relationship between the relative peak width (W) and pH is given by: W = -12.731pH + 31.75.

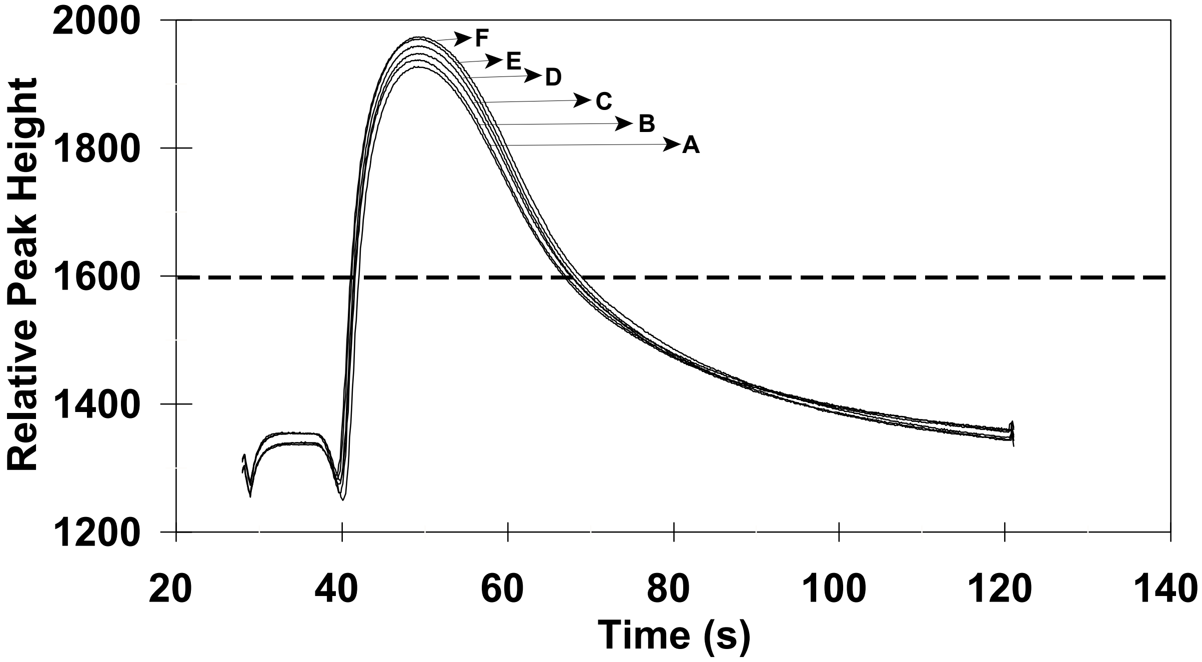


Figure 5 SI titration peaks of different HCl standard solutions titrated with NaOH concentration of 0.001mol/l. HCl standards for the different peaks are: (A) 0.025; (B) 0.030; (C) 0.035; (D) 0.040; (E) 0.045 and (F) 0.050 mol/l.

Accuracy and Precision

The accuracy of the proposed system was first evaluated by comparing the results obtained with the SI system with those obtained from manual and automated titrations for two control standard samples. The results are given in Table 2. The process was then repeated in the process effluent environment to evaluate the feasibility of the method with that of an automated batch and manual titration. The results of eight samples from process effluent streams, given in Table 4, revealed excellent comparability. The results in Tables 2, 3 and 4 gave an % RSD of less than 0.22 for the SI method which is far much better than those for the manual and automated titrations.

Table 2 Comparison of results of standard control samples obtained by the proposed SI titration system with standard manual and automated batch titration methods[a].

Standard Control Samples	SI titration		Manual		Automated	
	(mol/l)	% RSD	(mol/l)	% RSD	(mol/l)	% RSD
Sample 1	0.02941	0.16	0.02863	0.34	0.02866	2.19
Sample 2	0.04665	0.16	0.0481	0.38	0.04812	0.41

[a] n = 10

Table 3 Precision of the proposed SI system.

Standard	% RSD (n = 10)
0.025 mol/l	0.13
0.030 mol/l	0.15
0.035 mol/l	0.08
0.040 mol/l	0.17
0.045 mol/l	0.09
0.050 mol/l	0.11

Table 4 Comparison of results of process effluent stream samples obtained by the proposed SI titration system with standard manual and automated batch titration methods[a].

	SI titration		Manual		Automated	
	(mol/l)	(% RSD)	(mol/l)	(% RSD)	(mol/l)	(% RSD)
Sample 1	0.03655	0.12	0.03691	0.256	0.03777	0.418
Sample 2	0.03413	0.078	0.03409	0.888	0.034778	0.314
Sample 3	0.03363	0.15	0.03418	0.234	0.03368	0.23
Sample 4	0.03128	0.13	0.03149	0.468	0.03218	0.358
Sample 5	0.03063	0.18	0.03031	0.242	0.03041	0.508
Sample 6	0.03061	0.22	0.03156	1.1	0.03196	0.5
Sample 7	0.0294	0.16	0.02826	0.335	0.02789	2.19
Sample 8	0.0466	0.16	0.04815	0.377	0.04843	0.409

[a] n = 10

Sample Frequency

It took 120 s to complete one cycle of a sample run, resulting in a sample frequency of 30 samples per hour. The % recovery was found to range between 95 and 106 % which satisfy the prerequisites set out for the analyser.

Statistical Comparisons

The comparison was done between the proposed SI titration process analyser and the standard manual and automated batch titration methods (Table 4). The comparison was done to establish whether the SI titration system can be accepted as giving reliable results for the titration of hydrochloric acid in the process effluent streams. The null hypothesis which assumes that the quantities from two different method are the same was used in order to check if the results from these methods will agree. The t-test with multiple samples (paired by differences) was applied to examine whether the two methods differed significantly at 95% confidence level. The null hypothesis is H_o: $\xi = 0$, against the alternative H_t: $\xi \# 0$, where ξ is the population paired difference[24]. The test is two tailed, as we are interested in both $0_d < 0$ and $0_d > 0$. The t-data paired test analysis was performed using the formula: $t_{calc.} = |0_D| \times \sqrt{n}/s_x$. The 0_D between SI and manual titration = -0.000265 and

s_x = 0.000813. The results between SI and automated titration was: 0_D = -0.00053 and s_x = 0.00107. For eight determinations, the degrees of freedom was 7 and at 95 % confidence level $t_{0.05,7}$ = 2.365 with the critical t-values being ±2.365. When substituting for $t_{calc.}$, it was found to be 0.922 and 1.400 respectively. Since all these values lies below the critical t-values , the proposed method can be accepted because the results are comparable at 95 % confidence level.

4. Conclusions

For the proposed sequential injection titration system, the peak profile were evaluated with the pH electrode as detector. The best response and peak shapes as well as precision were obtained for the acid-base configuration. The SI titration system is fully computerized, is cheap and has a minimum consumption of reagents which is less than in manual and automated as well as flow injection titration. The linear range is, however, limited but can easily be adjusted to suit the specific need by just changing the base concentrations. The results are excellent and comparable with the standard manual and automated batch titration methods.

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