

Process potentiometric sequential injection titrations

by

Mulalo Gift Mashamba

Submitted in partial fulfilment of the requirements for the degree

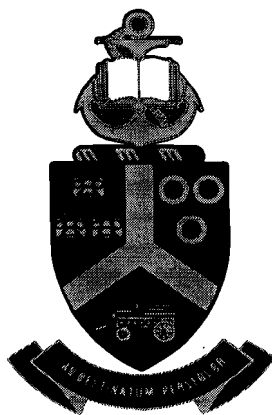
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Degree: Magister Scientiae

Synopsis

Interest in the automation of titration arise from the fact that many acid-base titrations in the process industries rely on manual titration which is time consuming. Miniaturization of these titration processes becomes attractive because of the reduced reagent consumption. These industries must produce higher quality products economically and in a friendly environment.

Due to its ease of automation, ability to handle concentrated solutions and simplicity, the application of sequential injection titration is an ideal tool in process effluent streams, food industries, beverage industries and production plants.

The sequential injection titration system was optimised with respect to all instrumental parameters of the system and applied for acid-base titrations. The results obtained showed high reliability and reproducibility. The system is fully computerised, inexpensive and suitable for on-line monitoring.

Proses potensiometriese sekvensiële inspuittitrasies

deur

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Samevatting

‘n Belangstelling om titrasies te outomatiseer, het ontstaan as gevolg van die groot aantal suurbasis titrasies in prosesindustrieë wat steeds op tydrowende handtitrasies steun. Miniatuursisteme van hierdie titrasieprosesse het aanloklik geword weens die vermindering in

reagensverbruik. Daar word verwag dat hierdie industrieë hoër kwaliteitprodukte ekonomies en omgewingsvriendelik sal produseer. As gevolg van die gemak waarmee dit geoutomatiseer word, geskiktheid om gekonsentreerde oplossings te hanteer en die eenvoud van die sisteem, is die aanwending van sekvensiële inspuittitrasie 'n ideale sisteem in prosesuitvloeirome, voedsel- en koeldrank- industrieë en produksie aanleë.

Die sekvensiële-inspuit titrasiesisteem is geoptimeer ten opsigte van al die instrumentele veranderlikes en aangewend vir suur-basis titrasies. Die resultate wat verkry is, toon 'n hoë betroubaarheid en reproduseerbaarheid. Die sisteem is ten volle gerekenariseer, goedkoop en geskik vir aanlynmonitering.

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Chapter 1

Sequential injection analysis

1.1 Introduction

Sequential injection analysis (SIA) is an analytical technique that was conceived from flow injection analysis [1,2]. This was due to the demand for mechanically simple and robust systems for process analysers that were able to process a large number of samples in a certain period of time. In contrast to FIA, SIA is based on discontinuous flow and consumes reagents only when the sample is being treated by exploiting a combination of stopped flow, reversed as well as forward flow in the microlitre scale [3].

The sequential injection system is assembled from the following: a pump, a multi position selection valve, a holding coil and an appropriate detector (Figure 1.1). The versatility of the sequential injection technique is centred around the selection valve where each port of the valve allows a different operation to be performed. Each port of the valve is dedicated to a specific purpose and the combinations of standards, reagents and detectors around the valve are easily modified to suit particular analysis [4].

The principle of SIA is based on sequential aspiration of a sample zone and reagent zone into a holding coil through a selection valve. The aspiration of zones is achieved by means of a pump which is capable of controlled stop-go-forward-reverse movement [5].

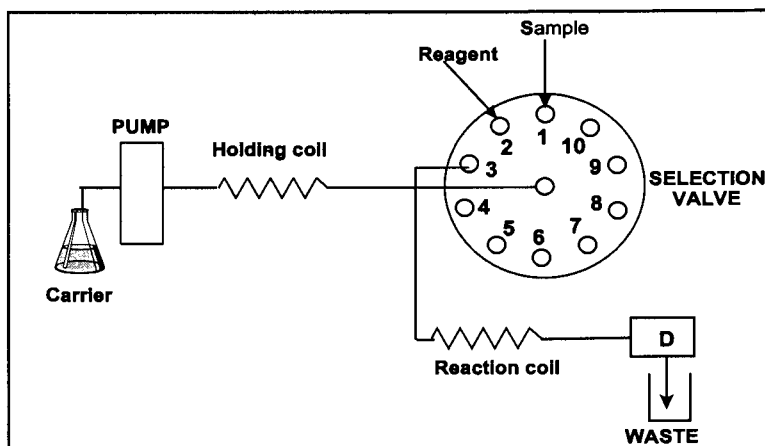


Figure 1.1 Schematic representation of a sequential injection analysis system (D-detector).

A stack of well-defined zones adjacent to each other are formed in the holding coil (Figure 1.2). The selection valve is then switched to the detector position and the flow reversal creates a composite zone in which the sample and reagent zone mutually disperse and penetrate each other due to combined axial and radial dispersion.

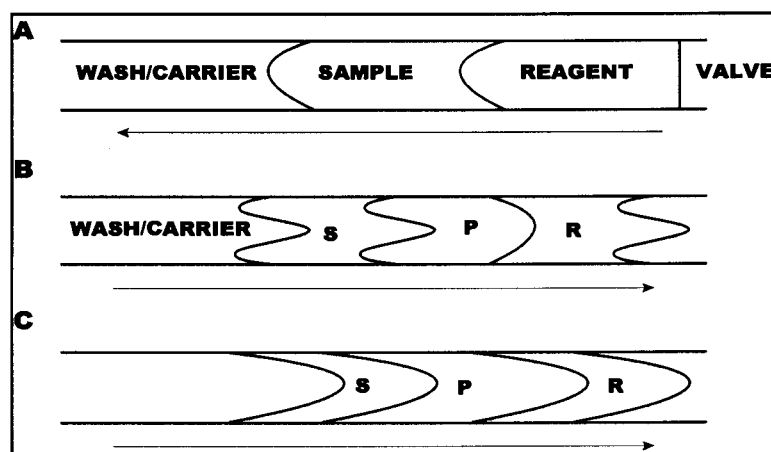


Figure 1.2 Principles of sequential injection analysis. Profile of zones after injection (A), immediately after flow reversal (B) and in reaction coil (C) S-sample R-reagent and P-formed product.

This creates the formation of a product zone which is monitored by the detector in the form of a peak whose height or width is related to the concentration of the species determined. The reagent is usually in excess to ensure effective mixing [6]. By varying the different operational parameters in a SIA flow conduit, it is possible to control the amount of dispersion within the system [7]. The order in which sample and reagent zones are stacked is in accordance with the reactions sought. The degree of mixing and the length of the reaction time as well as the sample and reagent volumes may be changed without physical re-configuration of the flow channel by means of programming the piston and valve movements [8,9]. Zone penetration was found to be the key parameter in the SIA system [7]. Its importance is ascribed to the fact that this influence has a dramatic impact on the surface area over which a concentration gradient exists and therefore over which axial mixing takes place [10,11].

The holding coil is considered the heart of the system as it substitute the mixing chamber and its volume could be adjusted by changing the length and diameter as required. A high reproducible flow pattern is obtained by computer control of the SIA system because an analytical procedure often requires a complex and high reproducible pattern. This technique can employ any detector capable of accepting a flowing stream. SIA uses a single channel pump to move the liquid in reverse and forward steps [12], as compared to a multichannel pump in FIA. Peristaltic pumps are preferred over syringe and sinusoidal flow types. The advantages of peristaltic pumps are: (i) configuration is easier and simpler to design, initiate and operate; (ii) they are widely available and easy to handle and (iii) the sampling cycle is considered shorter as there is no need for wash solution aspiration. Syringe pumps on the other hand offer a pulseless and highly precise flow but they require priming before use, and have a limited reservoir volume and are relatively expensive. This technique of SIA have the advantages of reduced

reagent consumption, easy and fast change of solutions and their handling and fast change of system parameters without changing the manifold.

1.2 Gradient techniques

Gradient techniques are based on the feasibility of a highly reproducible choice of a suitable element of fluid from the continuous concentration gradients formed at the interface between the dispersed sample zone and the carrier stream. Measurements are done on the initial or final portion of the resulting curve. Measurements in gradient techniques are usually executed under conditions other than the optimum for achieving maximum sensitivity [13]. The concentration gradient can be formed by injecting one or several zones which may result in either a single or a multiple peak which yields additional information on sample composition. The gradient approach yields the capability to perform procedures not feasible by conventional continuous flow analysis. The potential of this approach suggests that flow techniques are not restricted to providing convenient analytical methods but are becoming applicable means of solution handling and avoiding time consumption and an error producing step. The oldest of these gradient techniques are FIA titrations [14 - 16], although there was some technical advancement, the basic principles are still the same and they are discussed in chapter 2.

1.2.1 Gradient dilution

Gradient dilution has been used to accommodate highly concentrated samples within the dynamic range of detector. This also decrease the effect of foreign compounds. The principle behind is based on the utilization of points along the concentration profile other than the peak

maximum [17]. The nature of the physical process of dispersion on which flow systems are based will ensure that the response and the calibration curves obtained from data collected at fixed delay times are linear provided that the analytical readouts are always taken at exactly the same time after the point of injection. Linear relationships can also be found if the physical dispersion is accompanied by a chemical reaction provided that the reaction is linear in nature [18]. Three conditions should be fulfilled in order to preserve linearity [14]:

1. The detectors' response to the concentration of the measured species should be linear,
2. No inhibition caused by reaction products should occur,
3. The reagents should be in excess in the element of the fluid of interest to ensure complete reaction or to maintain the kinetic rates.

The advantage of this approach is that manual pre-dilution of samples material can be avoided and a large concentration range can be accommodated. Dilutions of up to 20 000-fold have been obtained for process control applications.

1.2.2 Gradient calibration

It is a logical extension of gradient dilution which relies on the strict reproducibility of physical dispersion accompanied by chemical reactions. The main goal is to avoid the usual repetitive calibrations by means of serially diluted solutions, as the information sought is contained within some of the segments of fluid originating from a sample zone of the most concentrated standard material. A multipoint calibration curve can be obtained from a single injection by identifying the time delay (Figure 1.3). Most conveniently the empirical formula $C = f(\text{delay time})$ is

obtained from a normal calibration evaluation.

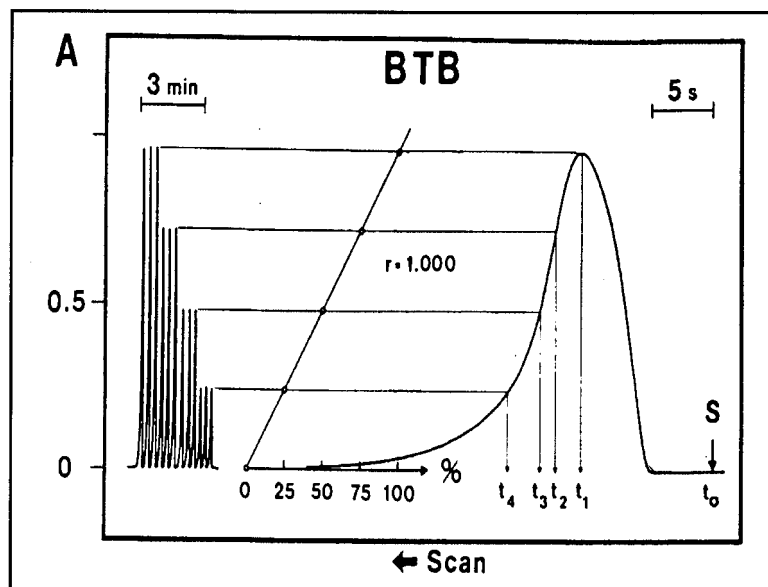


Figure 1.3 The principle of gradient calibration, showing on the left-hand side a conventional run where standards covering 25%, 50%, 75%, and 100% of the range were injected each in triplicate, and on the right-hand side a single injection of the 100% standard, which was recorded at high chart speed. Via a conventional calibration line ($r = 1000$), delay times t_1 , t_2 , t_3 , and t_4 are then identified, corresponding to known levels of originally injected standards [19].

1.2.3 Stopped flow

This method is achieved by intermittent pumping where the pump can be stopped and re-started at exactly controlled times. The reaction mixture is halted within the observation volume of the flow-through detector by stopping the flow and to measure the rate of change of the signal with time. This is accomplished by the combination of a suitable dispersion of the sample material within the reagent stream and on subsequent reaction-rate measurement, when the carrier is held

still. Stopping the sample zone in the cell allows the degree of reaction to be completed and stopping it before the cell increases residence time and therefore reaction time without adding dispersion. The assumption made is that the analytical reaction is continuing during the stopped-flow period. This technique compensates for variations in background signals produced by the potential interferences or differences in the sample matrix and also allows a fine adjustment of the reagent-to-sample ratio by choosing an appropriate delay time.

1.2.4 Gradient scanning

This was originally suggested by Janton and Ruzicka [20] providing convenient means of studying the chemical and physical phenomena which takes place when the solutions are mixed. The principle of this method is that a physical parameter is measured continuously within a certain range along the dispersed sample zone. The rate of scanning should be much faster than the movement of the carrier stream, so that the dispersed zone appears as to be stationary or the selected sections of the zone appears as to be stopped consecutively within the detector. Combination of gradient scanning and electronic dilution is seen as a logical extension of this approach.

1.2.5 Electronic calibration

This method relates the signal output to the concentration of a sample. This can only be achieved if there is an established relationship between the peak height, time of measurement and concentration of the sample. The advantages of this method are (i) fast calibration in the analysis of a large number of samples, (ii) higher precision and (iii) deviation caused by

chemical reaction are cancelled out during the sole standard running of calibration.

1.3 Aim of the study

Sequential injection analysis is a technique that has a tremendous potential for on-line processes measurements and in the monitoring of the environment.

Titration is the simplest and most commonly used method for volumetric analysis.

The combination of SIA and titration results in a hybrid technique which possesses advantages from both the SIA technique and the novelty and simplicity of the titration method.

The automated SI titration has great potential for exploitation in process analysers and other analysis systems.

In order to illustrate the potential of automated titration, the SI titration technique was used for the determination of acid concentration.

The application of sequential injection titration for environmental and food analysis was considered. This was exemplified by the determination of hydrochloric acid analysis, acetic acid and total acidity.

The determination of hydrochloric acid from process effluent streams was carried out by SI titration. Hydrochloric acid is a corrosive acid which is used as a disinfectant and pool cleaning.

In industries it is used in pickling of metals for dissolving scale and oxide films, extraction of ores, dissolution of rocks in crude oil drilling and for various processes in synthesis of organic products.

On-line dilution of samples may sometimes be necessary in acid determinations. Manual dilutions are often tedious, time and reagents consuming and are usually the source of experimental errors in routine laboratory analysis and process control. They are also undesirable for toxic samples. SI titration provided a solution to alleviate the disadvantages from the manual method. On-line dilution was applied in the determination of concentrated hydrochloric acid by SI titration.

Acetic acid is corrosive and is used in the manufacturing of solvents, synthetic fibres and plastics. It is also used in the household as an acidic seasoning and preservative. The determination of vinegar has a significance bearing on the health within the household as too much acid is detrimental to human health.

The determination of total acidity in soft drinks is essential because concentration causes severe health problems. The use of sequential injection titration with potentiometric detection was preferred in all the above mentioned analysis.

1.4 References

1. J. Ruzicka and G. D. Marshall, *Anal. Chim. Acta*, **237**, (1990), 329.
2. J. Ruzicka and G. D. Marshall and G. D. Christian, *Anal. Chim. Acta*, **62**, (1990), 1861.
3. J. Ruzicka, *Trends Anal. Chem.*, **17**, (1998), 69.
4. R. I. Stefan, J. F. van Staden and H. Y. Aboul-Einein, *Electrochemical Sensors in Bioanalysis*, (2001), Marcel Dekker, New York USA.
5. J. Ruzicka, *Anal. Chim. Acta*, **261**, (1992), 3.
6. T. Gubeli, G. D. Christian and J. Ruzicka, *Anal. Chem.*, **63**, (1991), 2407.
7. J. F. van Staden and A. Botha, *S. Afr. J. Chem.*, **51**, (1998), 100.
8. J. Ruzicka and T. Gubeli, *Anal. Chem.*, **63**, (1991), 1680.
9. N. W. Barnett, C. E. Leneham and S. W. Lewis, *Trends Anal. Chem.*, **18**, (1999), 346.
10. R. E. Taljaard, *Application of sequential injection analysis as process analysers*, M.Sc. Thesis, University of Pretoria, (1996).
11. J. F. van Staden, H. du Plessis, S. M. Linsky, R. E. Taljaard and B. Kremmer, *Anal. Chim. Acta*, **354**, (1997), 59.
12. A. Ivaska and J. Ruzicka, *Analyst*, **118**, (1993), 885.
13. M. Valcarcel and M. D. Luque de Castro, *Flow injection analysis: Principles and Applications*, (1987), Ellis Harwood, Ltd, Chichester, England.
14. S. Olsen, J. Ruzicka and E. H. Hansen, *Anal. Chim. Acta*, **136**, (1982), 101.
15. E. H. Hansen, *Fresenius Z. Chem.*, **329**, (1988), 656.
16. J. Ruzicka and E. H. Hansen, *Anal. Chim. Acta*, **145**, (1983), 1.
17. J. Ruzicka, E. H. Hansen and H. Mosbaek, *Anal. Chim. Acta*, **92**, (1977), 235.
18. A. U. Ramsing, J. Ruzicka and E. H. Hansen, *Anal. Chim. Acta*, **129**, (1981), 1.

19. J. Ruzicka and E. H. Hansen, *Flow Injection Analysis*, **62**, (1988), 2nd Ed. Wiley New York.
20. J. Janton and J. Ruzicka, *Anal. Chim. Acta.*, **139**, (1982), 105.

Chapter 2

Titration and potentiometry

2.1 Introduction

Analytical chemistry is concerned with the chemical characterization of matter, either quantitatively or qualitatively. In a modern industrialised society the analytical chemist has a very important role to play. Chemicals make up everything we use or consume, and knowledge of the chemical composition of many substances is important in our daily lives. Analytical chemistry plays an important role in nearly all aspects of life: environmental, manufacturing, clinical, agricultural, metallurgical, forensic and pharmaceutical chemistry. The quality of manufactured products often depends on proper chemical proportions, and measurement of the constituents is a necessary part of quality control. The need to quantify different chemical constituents from our immediate environment has led to the development of a variety of methods. These methods range from complex and expensive to simple and inexpensive procedures all striving to give reliable and accurate results. Having ascertained the nature of the constituents of a given sample, the analyst is then frequently called upon to determine how much of each component, or of specified components, is present. Such determinations lie within the realm of quantitative analysis. The different methods which are commonly used to achieve this purpose are gravimetric, electrogravimetric, titrimetric, volumetric, spectrophotometric and chromatographic. The choice of the method depends on the sample matrices and the quality of the results required.

2.2 Titrations

Titrimetric methods are generally used in analytical laboratories for quantitative analysis. Their popularity is due to the fact that they are convenient and the end point is distinctively detectable. They are used if a direct measurement does not yield acceptable results which is usually the case in the assay of acids and bases. Titrimetric methods are classified into gravimetric and volumetric techniques. Gravimetric titration involves the measurement of the concentration of the analyte as the percentage mass per volume. Volumetric titration involves measuring the volume of a solution of known concentration (titrant) needed to react completely with the analyte (titrand). The equivalence point is reached when the amount of added titrant is chemically equivalent to the amount of analyte in the sample.

Volumetric analysis represents a classical form of titration which are performed by slowly adding a standard solution from a burette or other volumetric measuring device to a solution with the analyte until the reaction between the two is complete. The actual volume delivered is calculated as the difference between the initial and final reading from any solution dispenser.

The equivalence point is reached when the amount of added titrant is chemically equivalent to the amount of analyte in the solution. The completion of the reaction between titrant and analyte is termed the end point. This end point may be determined by colour change imparted by either the titrant itself or the indicator.

An indicator may be a weak acid or base that is highly coloured or colourless. Each specific indicator undergoes a colour change at a particular range which is normally about two pH units.

This colour change interval varies widely with different indicators [1]. However the complexity of the matrices that are prevalent in industrial analysis has led to the development of other forms of titrimetric analysis with a variety of detectors.

The detection can also be achieved by measuring: (a) the potential between an indicator electrode and reference electrode (b) the change in electrical conductivity of the solution (conductimetric), (c) the current between an indicator electrode and a depolarized reference electrode (amperometric) or (d) the absorbance of the solution (spectrophotometric).

Potentiometric methods embrace two major types of analysis. The first one involves the direct measurement of an electrode potential from which the concentration of an active ion can be derived (direct potentiometry). The second one which dates back from the beginning of twentieth century is used for the location of the end points in the titrimetric methods of analysis (potentiometric titration). The method requires the use of reference electrode, an indicator electrode and a potential measuring device. The overwhelming importance of potentiometric titration is due to its high selectivity, precision and accuracy, the simplicity of the technique and the ample choice of electrodes [2].

Unless automated, titration equipment is usually less expensive, because the indication of the equivalence point does not require a very fine detector, as it is the point of maximum change in colour intensity, potential etc. which is being sought [3]. Three requirements must be fulfilled for a reaction to be the basis of titrimetric determination:

1. The reaction should essentially go to completion.

2. The reaction must proceed rapidly so that titration can be performed within a reasonable period.
3. The reaction must be unambiguous, so that a definite equivalence of the reactants exists.

The troublesome processes of collecting and plotting the data required for the titration curve, and the time-consuming operations stemming from the batch wise mode of performing titrations, are the main draw back of titrimetric procedures. The utilization of large amounts of reagents in the manual titration and the fact that it is tedious stimulated the research in automation of the titration procedure [4-7].

2.2.1 Automatic titrations

Modern automatic titrators allow the definition of complete analysis which achieves maximum flexibility in method development [8]. The performance of the titration can be controlled in a variety of ways:

- by use of empirical equations for the calculation of ΔV from preceding titration data points.
- by use of microprocessors to control volumetric equipment.
- by use of robot stations in implementing labourious manual methods or in handling toxic or hazardous substances.

An automatic titrator consists of a titrant delivery system, titration vessel, titration monitor and control section as shown in Figure 2.1 which all work together.

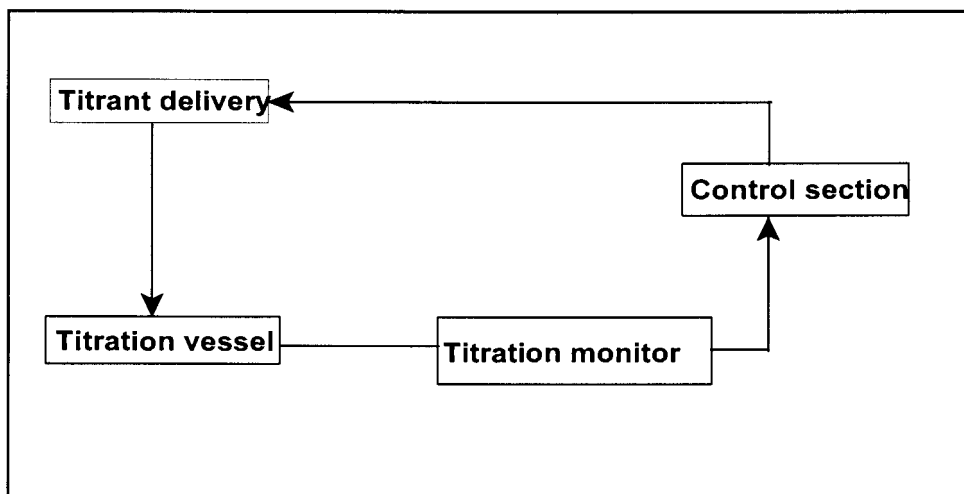


Figure 2.1 Components of an automatic titrator.

Some of the automatic titrators contain a sample changer which also helps to reduce the work load. Sampling and sample preparation also form part of the analytical procedure [8]. To significantly improve productivity, it is necessary to automate the whole process including sample transport and preparation. The automation of the titration system hinges on the manipulation of the titrant delivery part such as in volumetric or coulometric. They are usually burettes equipped with automatic valves or automatic syringes. Automatic syringe burettes are long, thin glass tubes with a volume scale equipped with a valve that can be operated automatically and in some cases there are facilities for automatic refilling and zero setting. The syringe burette resembles a medical syringe and the titrant can be dispensed at a preset rate. Most modern automatic titrators use the syringe burette. Figure 2.2 shows a titravalve with multiple titrant delivery using a single burette.

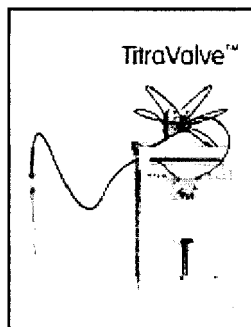


Figure 2.2 Picture of commercial TitraValve [9].

Constant-flow burettes overcome the problem of non-uniform rate of delivery arising from the use of ordinary burettes by keeping the hydrostatic pressure constant [10]. Titration vessels can be a simple beaker or titration cell, depending on the kind of monitoring system used. Figure 2.3 shows representative of commercial titration systems. They can be used for both titration and ion analysis.



Figure 2.3 Pictures of PC-Titrate (A) and QC-Titrate (B) [9].

The PC-titrate (Figure 2.3 A) is used with beaker, auto sample and it has four electrodes channels. The QC-titrate (Figure 2.3 B) on the other hand, is used with beaker and it has two electrode channels. Automatic titrators allows the rate of titrant delivery to be varied in such a way that mixtures of several species with similar dissociation or stability constants can be

titrated with good resolutions. The instrument covers the whole range of potentiometric methods such as acidimetric, redox, precipitation, complexometric and non-aqueous titrations. Although the piston burette allows reproducible titrant addition and sensors replacing the colour indicator, many automated titrimetric procedure are still based on batch operation, which requires relatively complicated ancillary units to facilitate sample introduction (burettes), draining and washing of the titrant vessel, and usually replenishing the titrant in the delivery unit.

2.2.2 FIA titrations

FIA titration is the oldest gradient technique [3]. Although there was some technical advancement, the method remained the same. For a sample zone of an acid which is injected into a carrier stream of base, the dispersed zone will become gradually neutralized by the base penetrating through the interfaces with the carrier stream at the leading and tailing boundaries (Figure 2.4).

Within these two boundaries an element of fluid can be found within which the acid is exactly neutralized by the base. These two equivalence points form a pair (A and B), having the same dispersion, and their physical distance (Δt) at constant flow rate will increase with increasing concentration of the base in the carrier stream.

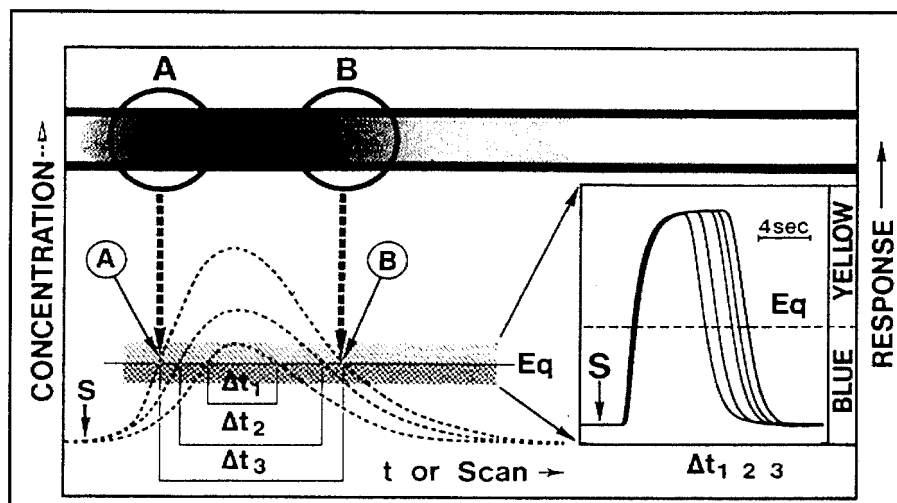


Figure 2.4 Flow injection titrations. The dispersed zone (top left) contains two equivalence points (*A* and *B*), the distance between them, Δt , being proportional to the acid concentration in the injected sample zone. By selecting the indicator, the equivalence level (*Eq*) is set and in this way decreasing values of Δt are obtained for decreasing concentrations of injected acid. Actual titration curves are shown on the right [11].

In all peak width measurements, the concentration dependence of the time span Δt depends on the concentration profile formed by the dispersion of the zone on the way from the injector to the detector. As long as the concentration profile conforms with the “one mixing stage” model, Δt as a function of the concentrations of acid and base will be given by the equation:

$$\Delta t = \frac{V_m}{Q} \ln 10 \log C_A^\circ - \frac{V_m}{Q} \ln 10 \log C_B + \frac{V_m}{Q} \ln 10 \log \frac{S_v}{V_m} \quad (1)$$

where C_A° is the concentration of the injected sample, C_B is concentration of the base, V_m is the volume of the mixing chamber, Q is the flow rate of the carrier stream, S_v is the volume of the

injected sample and n is the stoichiometric factor of the reacting components. If a constant sample volume is injected into a single-line system, the equation becomes:

$$\Delta t = k_1 \log C_A^\circ + k_2 \quad (2)$$

where k_1 and k_2 are constants and which through calibration with a series of known standards directly yields the result from the recorded peak width read. Although the use of a mixing chamber in FIA titrations results in higher precision [12], the larger volume of the chamber is undesirable because it results in a larger dispersion of the sample material causing the loss of sensitivity as well as low sampling throughput if a moderate reagent consumption is to be maintained. Ramsing *et al* [11] undertook an investigation in order to eliminate this drawback by implementing a high-speed titration instead of mixing chamber. They were called “high-speed” titrations because the sampling frequency was far much greater than that for a gradient chamber. The injection process itself conforms with the “one-mixing-stage” model which allows miniaturization and simplification of the FIA system [11]. FIA titrations can be used either as a single line system or a two line system.

Potentiometric FIA titration has been developed [3] where the ion-selective electrodes yield a logarithmic response and thus encompass a wider concentration range than do colour indicators. The curves produced exhibit an S-shaped form. Each titration is initiated by an abrupt increase in potential which is then followed by S-shaped descending part. The inflection point marks the end point of the titration. Δt is read off at fixed potential and is later plotted against the concentration of the injected sample. A straight line is found and the slope of the resulting curve depends on the flow rate. The main drawback of FIA titrations is that they have very high

sample or reagent consumption. Ruzicka and Hansen [13] formulated this rule on titration:

“All FIA titrations are based on peak width measurements but not all peak width measurements are FIA titrations. The difference is that FIA titrations are based on location of a pair of equivalence points by using indicator or self indicating chemical reactions, while peak width measurements rely on a time of flight of a dispersed zone measured at a selected level of detector response”.

2.2.3 SIA Titrations

SIA titrations were first introduced in 1997 by van Staden and du Plessis [14]. The concept is based on the sequential aspiration of a base titrant, acid analyte and a second base titrant zone into a distilled water carrier stream. This gives a stack of well-defined zones adjacent to each other in a holding coil and swept by flow reversal through a reaction coil to the detector. The dispersed sample zone becomes gradually neutralized by the base penetrating through interfaces. The acid sample zone is completely covered by the two adjacent base zones (Figure 2.5). At the front and the tail of the sample an element of fluid exists within which the acid is exactly neutralized by the base [14,15]. The two equivalence points form a pair, having the same dispersion and their physical distance will increase with increasing concentration of the injected sample as in flow injection titration systems. A linear relationship between peak width and logarithm of acid concentration can be obtained. Other linear ranges are possible by changing the titrant concentrations.

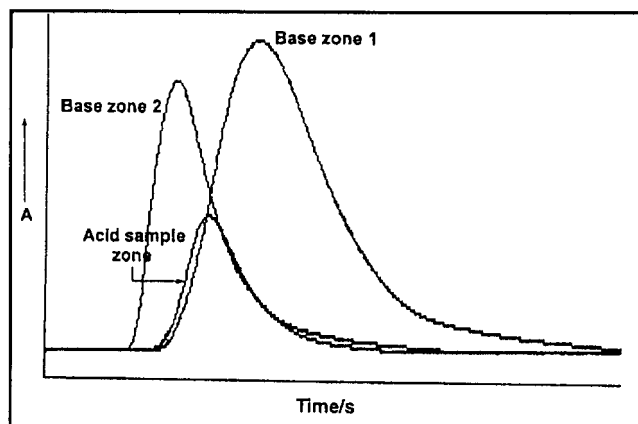


Figure 2.5 Peak profiles visualizing the amount of dispersion and zone penetration.

Sultan *et al* [16] used SI titration with spectrophotometric detection for the assay of vitamin C in pharmaceutical products. The method is based on the oxidation of vitamin C by cerium (IV) solution in sulfuric acid media and the peak monitored at 410 nm. A sequential injection titration of weak and strong acids on which peak area was measured was described by Maskula *et al* [17]. This method is based on sequential aspiration of an acidic sample zone and only one base zone into a carrier stream of distilled water. The peak area of unneutralized base is recorded by an LED-spectrophotometer and found to be proportional to the logarithm of the acid concentration.

2.3 Electrodes

An electrode is a device, made of specific materials that is in contact with an ionic conductor. It is used in the modification of electrolyte (ionic conductor) by applying the electric potential to the electrode or to measure the potential of the electrolyte. The processes that occur at the electrodes are redox reactions which involves the transfer of charge from the electrode to the

dissolved species in solution or vice versa. A net change in the number of free electrons is accommodated by the metallic bond in electrode. The positively charged ions usually dissolve in the solution leaving the electrons delocalized throughout the electrode, and the solution becomes positively charged or in the reverse where the ions in the solution take electrons from the electrode before depositing on the surface leaving the electrode deficient of electrons and being positively charged. This result in the formation of the interface between the electrode and the electrolyte. The interface formed may be an electrical double layer which consists of a sheet of positive charge at the surface of electrode and a sheet of negative charge in solution or vice versa. The exact structure of the double layer depends on the electrode material and the composition of the solution contacting it [18]. The classification of electrodes is given below:

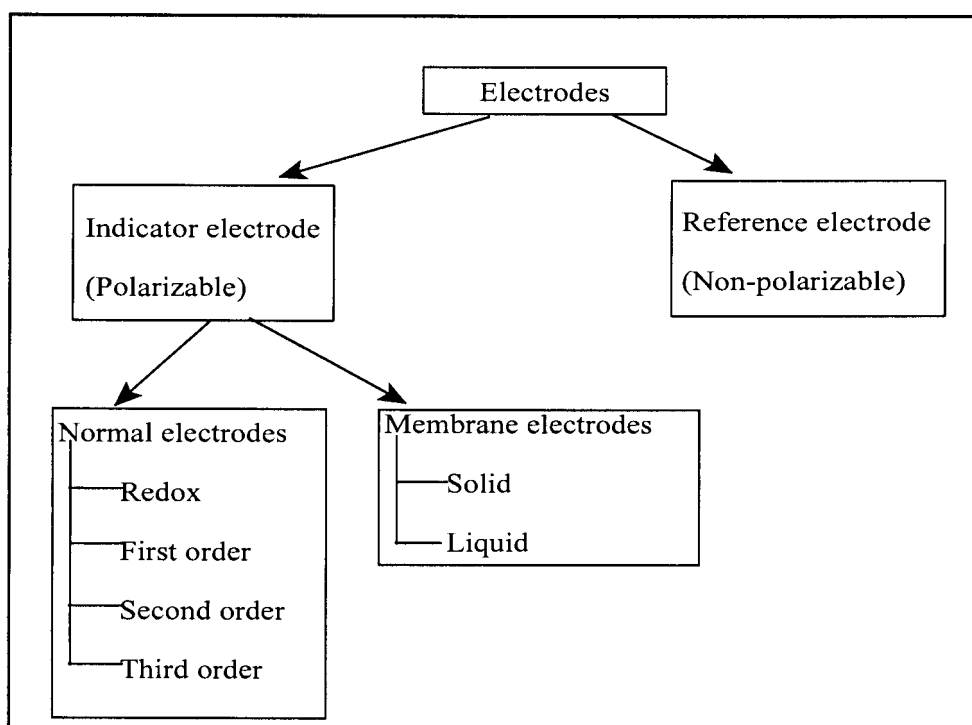


Figure 2.6 Classification of electrodes.

Normal electrodes are electrodes in which the solid part of the interface is an electronic conductor and electron transfer is responsible for the potential difference. They are generally used in polarography, electro gravimetry and faradaic techniques. They are subjected to contamination and interference by redox agents.

2.3.1 pH Glass electrode

The electrode consists of a pH-sensitive glass bulb that acts as a membrane between an inner reference electrolyte and the test solution. The glass membrane is the key to the selectivity of the electrode. The potential developed between the surface of a glass membrane and a solution is a linear function of the pH of the solution. A small volume of dilute hydrochloric acid with silver chloride solution is contained in the tube or a buffer containing chloride ions in some electrodes. Figure 2.6 shows a typical combined pH glass electrode.

Ion exchange occurs between sodium ions from the glass and hydrogen ions from the test solution so that the surface layers become more or less acidic. This result in direct predominant ion exchange of hydrogen ions from the test solution towards the gel surface, giving it a positive potential difference versus the test solution.

The surface of the glass membrane needs to be hydrated prior to its usage. This is done by soaking the electrode in water for a longer time so that the cations are free to exchange with the external solutions or in order to have pH activity. The anion sites are covalently bonded to the bulk of glass and fixed. This result with the cation being free to exchange with the external solutions.

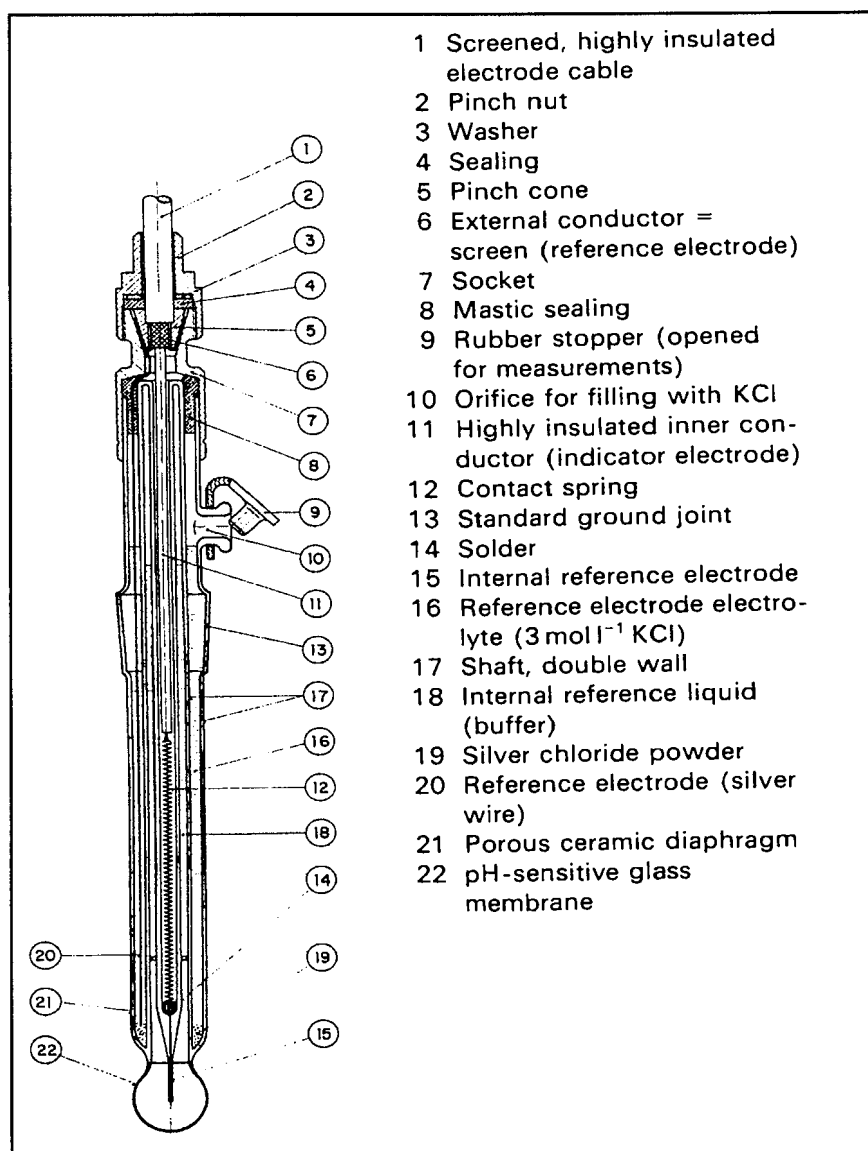


Figure 2.7 Cross section of a combined pH glass electrode (Metrohm).

The lifetime of pH electrodes is strongly dependant on the measuring conditions, such as temperature which reduces their lifetime. The temperature must be controlled and maintained at a constant value during measurements where 298 K is generally recommended for the characterization of the electrodes [19]. The surface of electrodes deteriorates with time due to adsorption of species from the solution or chemical changes to the surface itself. This results

in variation of the sensitivity or complete inhibition of charge transfer [20]. Contamination of the internal electrode solution and / or test solution where interfering species diffuse across the membrane from the test solution into the internal solution can also affect the performance of the electrodes. Electrodes are usually stabilised by potassium chloride and potassium sulphate.

2.4 Potentiometry

This is the measurement of ionic activities and concentrations via the measurement of electrochemical potential. It is a technique that can be used to follow the progress of a chemical reaction. The measurement is done in the absence of appreciable currents without disturbing the equilibrium at the sample-membrane interface. A reference electrode, indicator electrode and a potential measuring device are used. The reference electrode must have a constant potential which is insensitive to the composition of the test solution. This potential must not depart from its equilibrium value when current demands are made upon it. Most commonly used reference electrodes are calomel and silver/silver chloride electrodes. The silver/silver chloride electrode is preferred over calomel electrode because it can resist temperatures of up to 60°C and also mercury(II) ions in calomel electrode react with fewer sample components than silver ions. Indicator electrodes are working electrodes that indicate by means of its potential the concentration of an ion in solution. It is employed in conjunction with the reference electrode and its response depends on the analyte concentration of a specific species.

A junction potential is always involved at the boundary between two dissimilar solutions or solids. It occurs when mobilities of positive and negative ions diffusing across the boundary are unequal. In most cases the junctions of different solution are found between the filling

solution of the reference electrode and the test solution. The filling solution should be nearly equitransferent where its cation and anion possesses almost equal transference numbers. In general, both electrolyte concentration and the ionic strength within the junction should be higher than ion concentrations in the sample solution. For example saturated potassium chloride solution or potassium nitrate are used where a mixture of potassium ions, sodium ions, nitrate and small amount of chloride minimizes the liquid junction potential [1].

In potentiometry it is necessary to work at the same ionic strength, to avoid the differences in the potential readings which can cause errors due to variations of the activity coefficients of the ions in the solution [21], or ion adsorption on the walls which can result in concentrations being overestimated. Strong electrolytes (ionic strength adjusting salts) are added into both the standard and sample solutions before measurements. However, the electrolyte must not form complexes with the sensed ion or contain species that can cause an interference in the response itself [22]. Strong electrolytes that are mostly used are sodium chloride, potassium chloride and some of the buffers.

Direct potentiometry involves the preparation of calibration curve with a standard concentration and the placement of the ion selective and reference electrodes in sample solution and the measurements are made in much the same way as pH measurements. It is the simplest method of all for the use of ion selective electrodes. Potentiometric titrations on the other hand are for reactions that goes to completion in order to indicate the end point and so do not need calibration.

2.4.1 Potentiometric titrations

These are titrations that involves measurement of potential of a cell that develops during the step by step addition of titrant into the sample. Modern instruments are able to monitor the potential and regulate the addition of titrant from a burette. The potential change is followed while other parameters are held constant. This change is slow at the beginning of the titration and increases to a maximum as the equivalence point is reached but reduces after passing the equivalence point. The results are plotted from cell potential as a function of the volume of titrant and have the familiar sigmoid or S-shape (Figure 2.8 Curve A). The equivalence point is indicated at the steepest point of the curve where the potential changes rapidly, which is the maximum rate of change of potential per unit volume. An equivalent volume at the end point is defined, V_e

$$C_s V_e = C_1 V_1 \quad (3)$$

where C_s is the concentration of standard, V_e is the end point volume of titrant, C_1 is the unknown concentration and V_1 is the volume of the unknown. When the point of maximum slope is not obvious such that the inflection point cannot be the end point, the precise results can be gained from the plot of first and second derivative (Figure 2.8 Curves B and C). The first derivative curve is obtained by adding the titrant solution in small, equal increments and plotting the difference between two consecutive potential readings as a function of the volume of titrant and the maximum is taken as the end point (Figure 2.8 Curve B). In the case where the first derivative does not show the end point clearly, a second derivative curve is used. This is obtained by plotting the difference between two consecutive differences versus the volume of the titrant solution added and the end point corresponds to the passage of the curve through zero

line (Figure 2.8 Curve C). Many types of titrations can be effected potentiometrically, e.g, acid-base, precipitation, complexation and redox titrations.

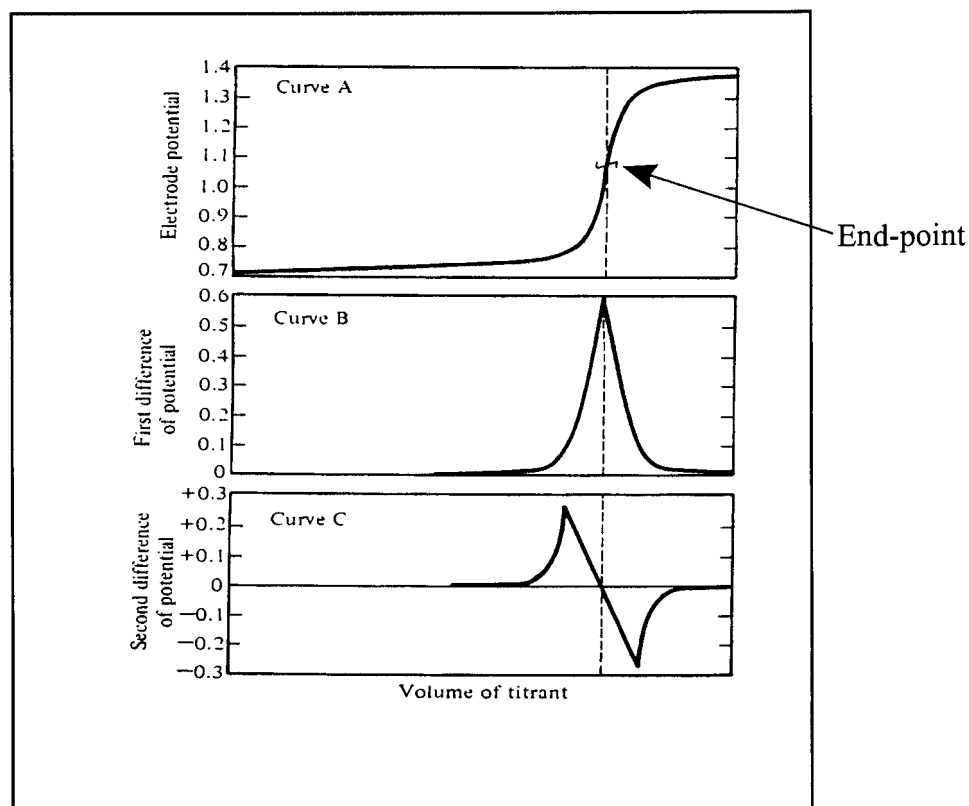


Figure 2.8 Curve A is an experimental potentiometric titration curve, Curve B is the first derivative curve of A and Curve C is the second derivative curve of A.

2.4.1.1 Acid-base titrations

The end point is determined by plotting the curve of pH versus the volume of acid or base added (Figure 2.8 Curve A). The point of maximum slope is taken as the end point. A pH meter together with a glass electrode is used to follow the pH changes during the titration. These titrations are used when the end point is difficult to observe due to coloured solutions [23].

2.4.1.2 Precipitation titrations

This are titrations that depends upon the combination of ions with no change in oxidation state. The ion concentration is determined by the solubility product of the sparingly soluble material formed during the titration at the equivalence point. The ion is precipitated by the addition of reagent and its concentration and potential of an indicator electrode changes rapidly in the region of the end point. An example is the titration of silver nitrate with sodium chloride by means of a silver electrode as an indicator electrode and a double junction calomel electrode as a reference electrode.

2.4.1.3 Complexation titrations

These are reactions that involves formation of soluble complexes with an excess of reagent. The most used reagent is ethylenediaminetetraacetic acid in which the four carboxylate functional groups as well as the two amine nitrogens, participate in bond formation with metal ions. This method is usually applied in the determination of calcium and magnesium ions in water.

2.4.1.4 Redox titrations

The potential of the electrode is controlled by the ratio of the oxidized and reduced species concentration. During the redox reaction of the reducing agent, the ratio changes more rapidly in the vicinity of the end point of the reaction. Titrations of this nature are characterized by titration curves with sudden change in potential at the equivalence point. The indicator electrode is usually a platinum wire or foil.

Potentiometric titrations are of importance because they generally offer an increased accuracy and precision. Accuracy is increased because measured potentials are used to detect rapid changes in concentration that occur at the equivalence point of titration. The influence of liquid junction potential and activity coefficients is minimized and the method enables a large number of species to be measured. Potentiometric detectors can easily be incorporated into the conduits of the flow system to form a simple, low-cost analyser. They offer the advantages of not tempering with the sample concentration when the moving sample is in contact with the electrode surface. The electrode surface is renewed by on-line polishing with the carrier. The diffusion layer helps to improve the linear concentration range, the sensitivity and the response time of electrode.

2.5 References

1. G. H. Jeffrey, J. Bassett, J. Mendham and R. C. Denney, *Vogel's textbook of quantitative chemical analysis*, (1978), 5th Ed., Longman group UK.
2. E. A. M. F. Dahmen, *Electroanalysis: theory and applications in aqueous and non-aqueous media and in automated chemical control: Techniques and instrumentation in analytical chemistry*, (1986), 7, Elsevier science, Amsterdam.
3. J. Ruzicka, E. H. Hansen and H. Mosbaek, *Anal. Chim. Acta.*, **92**, (1977), 235.
4. R. Hoogendijk, *Anal. Chim. Acta.*, **378**, (1999), 211.
5. J. I. Partanen and P. M. Juusola, *Fluid phase equilibria*, **173**, (2000), 135.
6. R. A. S. Lapa, J. L. F. C. Lima, R. Perez-Olmos and M. P. Ruiz, *Food Control*, **6**, (1995), 155.
7. P. Pillay, D. Barnes and J. F. van Staden, *Anal. Chim. Acta.*, **440**, (2001), 45.
8. C. De Caro, *G. I. T. Laboratory Journal*, **3**, (2000), 160.
9. MAN-TECH Associates, 2001, USA
10. M. Valcarcel and M. D. Luque de Castro, *Automatic methods of analysis: Techniques and instrumentation in analytical chemistry*, (1988), 9, Elsevier Amsterdam.
11. A. U. Ramsing, J. Ruzicka and E. H. Hansen, *Anal. Chim. Acta.*, **129**, (1981), 1.
12. J. Ruzicka and E. H. Hansen, *Flow injection analysis*, (1988), **62**, 2nd Ed, Wiley New York.
13. J. Ruzicka and E. H. Hansen, *Flow injection analysis*, (1981), **62**, Wiley New York.
14. J. F. van Staden and H. du Plessis, *Anal. Comm.*, **34**, (1997), 147.
15. J. F. van Staden and H. du Plessis, *Talanta*, **52**, (2000), 83.
16. S. M. Sultan, Y. A. M. Hassan and K. E. E. Ibrahim, *The Analyst*, **124**, (1999), 917.

17. S. Maskula, J. Nyman and A. Ivaska, *Talanta*, **52**, (2000), 91.
18. D. Malan, *Arrays of crystalline membrane ion-selective electrodes in flow injection potentiometry*, (1997), MSc-Thesis, University of Pretoria.
19. R. I. Stefan, J. F. van Staden and H. Y. Aboul-Einein, *Electrochemical sensors in Bioanalysis*, (2001), Marcel Dekker, New York USA.
20. M. C. Matoetoe, *Development and characterization of a flow system for voltammetric analysis*, (1998), PhD-Thesis, University of Pretoria.
21. F. Battaglini, E. J. Calvo, C. Danilowicz and A. Wolosiuk, *Anal. Chem.* **71**, (1999), 1062.
22. V. V. Cosofret and R. P. Buck, *Pharmaceutical applications of membrane sensors*, (1992), CRC Press Inc. Boca Raton, Florida.
23. H. A. Flaschka, A. J. Barnard Jr and P. E. Sturrock, *Qualitative Analytical Chemistry*, (1980), 5th Ed., Willard Grant Boston.

Chapter 3

On-line determination of hydrochloric acid in process effluent streams by potentiometric sequential injection acid-base titration

3.1 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 system is that it is 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 analysed at the other tower. The author reported 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 stream of the flow injection titration system with two titrant zones on either side of the sample zone in distilled water carrier stream. The system was expanded to the determination of sulphuric acid in process effluent streams from 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 0.025 and 0.05 mol/l and that it should be able to screen higher acid concentration with an alarm system in order to warn the production plant that the environmental limit has been exceeded. SIA seemed to be an ideal system for such an analyser and was adopted for this purpose. The spectrophotometric detection previously used was replaced by a pH electrode [21,22].

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 neutralised 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 form a pair, having the same dispersion, and their physical distance will increase with increasing concentration of the injected sample.

3.2 Preparation, properties and utilisation of hydrochloric acid

Hydrochloric acid is a solution of the gas hydrogen chloride in water. Hydrogen chloride gas can either be derived from the burning of chlorine and hydrogen or co-produced during a variety of chemical reactions involving chlorine or its compounds with hydrogen containing materials. It is then absorbed in water in an absorption tower usually manufactured in graphite. The acid varies from colourless to pale yellow according to purity. This acid evolves hydrogen chloride vapour with its characteristic sharp irritant odour and the amount of vapour is primarily dependent on the acids' strength, turbulence and temperature. It is stable under room temperature and normal atmospheric pressure.

It is highly corrosive and attacks most common metals, including iron, steel and lead liberating the flammable gas hydrogen. It also destroys many common clothing materials. When hydrochloric acid is released in the soil, it is not expected to bio-degrade and may leach into the ground water. It is toxic to aquatic life, and humans. When inhaled causes coughing, choking, inflammation of the nose and throat. When hydrochloric acid comes into contact with the skin it causes redness, pain and severe skin burns.

Hydrochloric acid is one of the most widely chemicals used in the manufacturing industry and synthetic chemistry. It is involved in the production of most of the everyday articles, but its principal applications include metal pickling, gelatine, dyestuffs, casein, pharmaceuticals, synthetic rubber and metal chlorides manufacture. Large amounts of hydrochloric acid are used in effluent treatment, regeneration of ion exchange resins and water treatment for swimming pools.

3.3 Experimental

3.3.1 Apparatus

The basic sequential injection system (SIA) is illustrated in Figure 3.1. It was constructed from a Gilson Minipuls 3 peristaltic Pump (Villiers-le Bel, France), a 10-port electrically actuated selection valve (Model ECSD10P, Valco Instrumentation, Houston, Texas, USA) and a pH electrode (Hamilton, Switzerland) connected to an Orion Research Microprocess 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 through out for device control and data acquisition. Tygon tubing was used for the construction of the holding coil (HC) and the reaction coils (RC). The length and diameter of the tubing used are indicated in Figure 3.1.

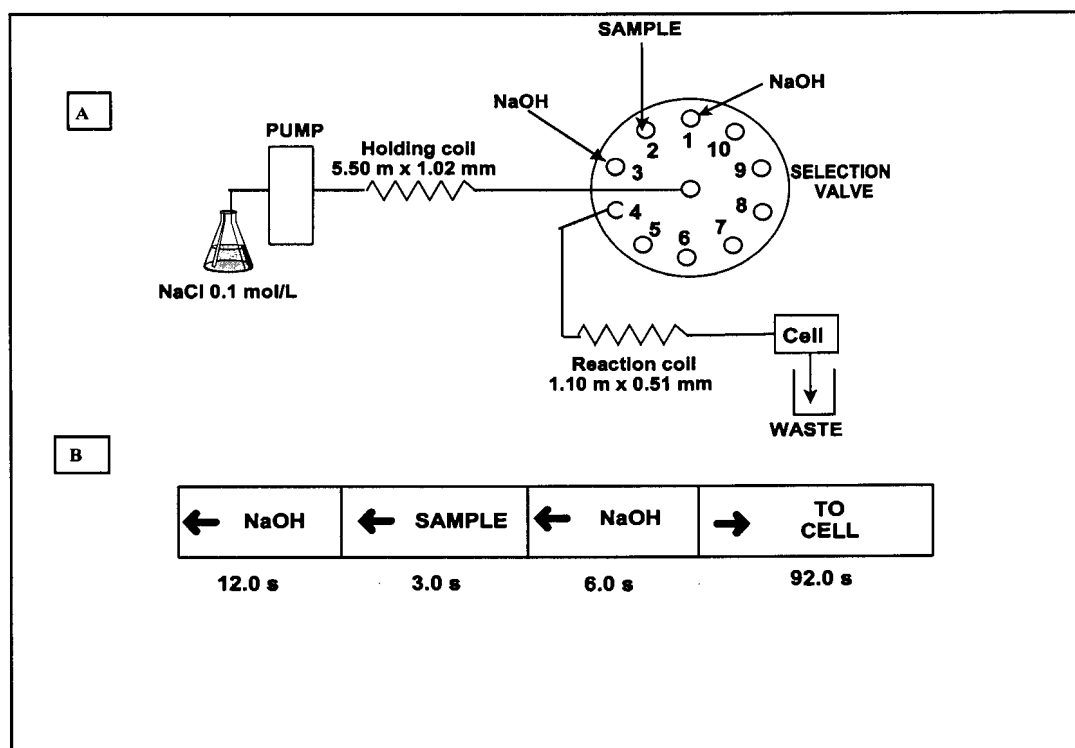


Figure 3.1 (A) Schematic representation of sequential injection titration system.
 (B) Device sequence for one cycle.

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.

3.3.2 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 solutions and dilutions.

3.3.2.1 Sodium chloride solution

A 0.1 mol/l sodium chloride 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.

3.3.2.2 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).

3.3.2.3 Hydrochloric acid standard solutions

Standard hydrochloric acid solutions in the range 0.025 to 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.

3.3.2.4 Samples

Effluent samples downstream from a hydrochloric acid production plant were directly analysed on the system without any sample pretreatment. The system was tested on-site to see if it fulfill the requirements of the factory.

3.3.3 Procedure

Table 3.1 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. 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 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 a 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 sodium hydroxide solution, valve position 2 for the standard or sample line and valve 9 for the second sodium hydroxide 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 3.1 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

3.4 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-site 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 where after the well defined stack of zones were channelled through a reaction coil to an 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 was discussed previously [21,22].

3.4.1 Optimization

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

3.4.1.1 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 percentage RSD is given in Figure 3.2.

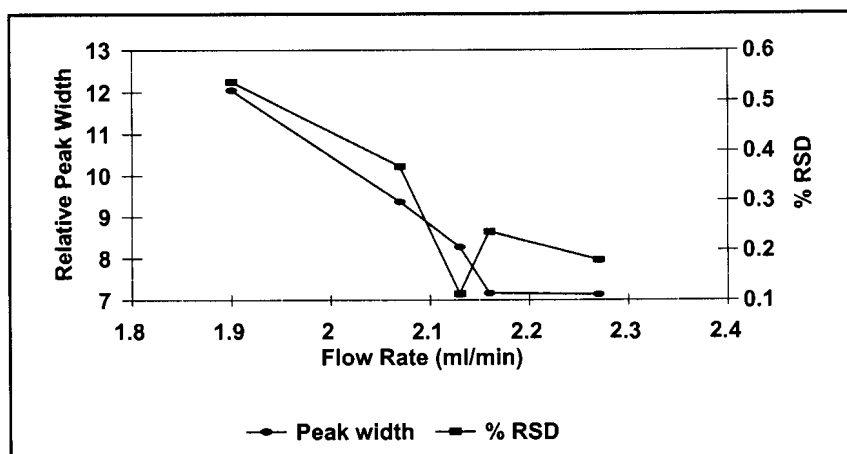


Figure 3.2 Influence of the carrier stream flow rate on peak width and percentage RSD ([NaOH] = 0.001 mol/l; [HCl] = 0.03 mol/l).

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 increase in flow rate as outlined in Figure 3.3. 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.

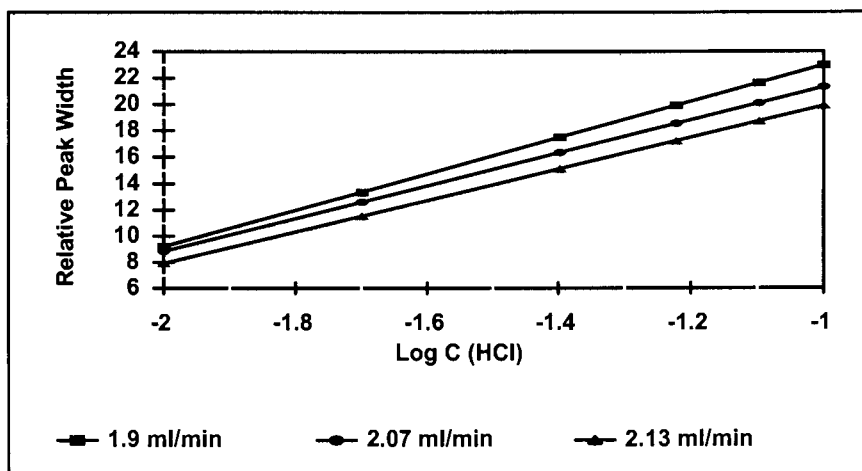


Figure 3.3 Calibration curves at different carrier stream flow rates ($[\text{NaOH}] = 0.001 \text{ mol/l}$).

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.

3.4.1.2 Sodium hydroxide concentration

The resulting relative peak width decreased with an increase in the concentration of the base as illustrated in Figure 3.4. The linear range was also affected by the base concentration. A concentration of 0.001 mol/l solution was chosen for the proposed method.

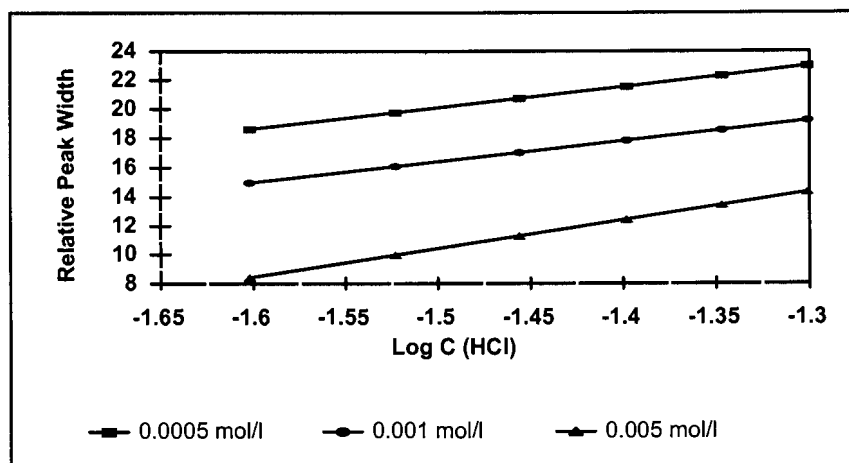


Figure 3.4 Influence of base concentration on peak width and linearity.

3.4.2 Method evaluation

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

3.4.2.1 Linearity

The SI titration peaks for different acid concentrations are shown in Figure 3.5. The dotted line indicates the height at which the peak width of the peaks were 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: $W = -12.731\text{pH} + 31.75$.

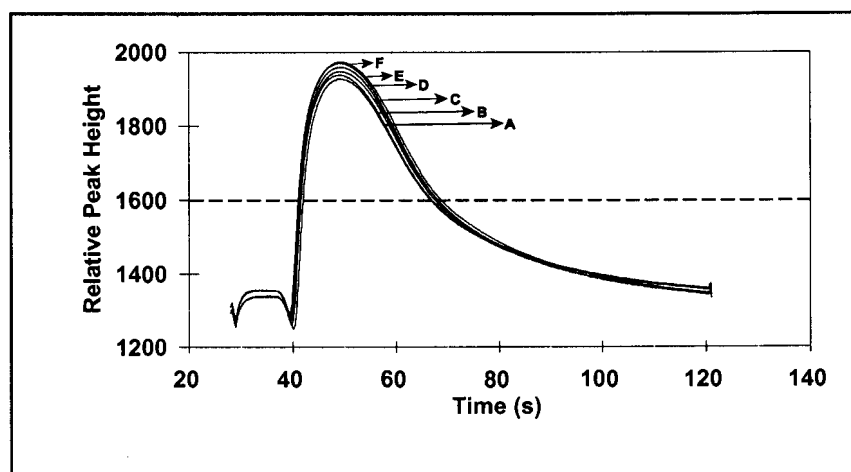


Figure 3.5 SI titration peaks of different hydrochloric acid standard solutions titrated with a sodium hydroxide solution ($[\text{NaOH}] = 0.001 \text{ mol/l}$). The concentration of hydrochloric acid standard solutions are: (A) 0.025; (B) 0.030; (C) 0.035; (D) 0.040; (E) 0.045 (F) 0.050 mol/l.

3.4.2.2 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 3.2.

Table 3.2 Comparisons of results of standard control samples obtained by the proposed SI titration system with standard manual and automated batch titration methods*.

Standard Control Samples	SI titration		Manual		Automated	
	(mol/l)	% RSD	(mol/l)	% RSD	(mol/l)	% RSD
Sample 1	0.0294	0.16	0.0286	0.34	0.0287	2.19
Sample 2	0.0467	0.16	0.0481	0.38	0.0481	0.41

* n = 10

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 3.3, revealed excellent comparability. The results in Tables 3.2, 3.3, and 3.4 gave an percentage RSD of less than 0.22 for the SI method which is far much better than those for the manual and automated titrations.

Table 3.3 Comparisons of results of process effluent stream samples obtained by the proposed SI titration system with standard manual and automated batch titration methods*.

Samples	SI titration		Manual		Automated	
	(mol/l)	% RSD	(mol/l)	% RSD	(mol/l)	% RSD
Sample 1	0.0366	0.12	0.0369	0.26	0.0378	0.42
Sample 2	0.0341	0.08	0.0341	0.89	0.0348	0.31
Sample 3	0.0336	0.15	0.0342	0.23	0.0337	0.23
Sample 4	0.0313	0.013	0.0315	0.47	0.0322	0.36
Sample 5	0.0306	0.18	0.0303	0.24	0.0304	0.51
Sample 6	0.0306	0.22	0.0316	1.1	0.032	0.5
Sample 7	0.0294	0.16	0.0283	0.34	0.0279	2.19
Sample 8	0.0466	0.16	0.0482	0.38	0.0484	0.41

* n = 10

Table 3.4 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

3.4.2.3 Sample frequency

To run the samples, it took 120 s to complete one cycle, resulting in a sample frequency of 30 samples per hour.

3.5 Statistical comparison

The comparison was done between the proposed SI titration process analyser and the standard manual and automated titration methods (Table 3.3). 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 methods 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 $H_0: \zeta = 0$, against the alternative $H_1 \neq 0$, where ζ is the population paired difference [24, 25]. The test is two tailed, as we are interested in both $\bar{x}_D < 0$ and $\bar{x}_D > 0$ where \bar{x}_D is the mean difference between the methods. The t-data paired test analysis was performed using the formula: $t_{\text{calc.}} = |\bar{x}_D| \times \sqrt{n} / s_x$. The \bar{x}_D between SI and the manual titration was -0.000265 with s_x (standard deviation) of 0.000813. The results between SI and automated titration was $\bar{x}_D = -0.00053$ and $s_x = 0.00107$. For eight determinations, the degree 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 $t_{\text{calc.}}$, 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.

3.6 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 inexpensive and has a minimum consumption of reagents as compared to the manual, automated and 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 compare excellently with the standard manual and automated batch titration methods but offering better average precision and very low percentage RSD.

3.7 References

1. C. De Caro, *GIT Laboratory Journal*, **3**, (2000), 160.
2. J. Ruzicka, E. H. Hansen and H. Mosbaek, *Anal. Chim. Acta*, **92**, (1977), 235.
3. A. U. Ramsing, J. Ruzicka and E. H. Hansen, *Anal. Chim. Acta*, **129**, (1981), 1.
4. D. R. Turner, S. Knox and M. Whitfield, *Anal. Proc.*, **24**, (1987), 360.
5. J. F. Tyson, *Anal. Proc.*, **24**, (1987), 362.
6. J. Toei, *Fresenius' Z. Anal. Chem.*, **330**, (1988), 484.
7. G. Naggy, Z. Feher, K. Toth, E. Pungor and A. Ivaska, *Talanta*, **26**, (1979), 1143.
8. Z. Feher, I. Kolbe and E. Pungor, *Analyst.*, **116**, (1991), 483.
9. B. Fuhrman and U. Spohn, *Anal. Chim. Acta.*, **282**, (1993), 397.
10. K. G. Schick, *Adv. Instrum.*, **39**, (1984), 279
11. N. Ishibashi and T. Imato, *Fresenius' Z. Anal. Chem.*, **323**, (1986), 244.
12. J. F. van Staden, *Water SA*, **12**, (1986), 93.
13. T. Imato, A. Katafuchi, T. Hamazoe, J. Yagi, K. Takahara and N. Ishibashi, *Anal. Sci.*, **5**, (1989), 777.
14. R. H. Taylor, J. Ruzicka and G. D. Christian, *Talanta*, **39**, (1992), 285.
15. R. H. Taylor, C. Winbo, G. D. Christian and J. Ruzicka, *Talanta*, **39**, (1992), 789.
16. A. O. S. S. Rangel and I. V. Toth, *Analyst*, **123**, (1998), 661.
17. P. B. Martelli, B. F. Reis, M. Korn and J. L. F. C. Lima, *Anal. Chim. Acta*, **387**, (1999), 165.
18. R. S. Honorato, M. C. U. Araujo, G. Veras, E. A. G. Zagatto, R. A. S. Lapa, and J. L. F. C. Lima *Anal. Sci*, **15**, (1999), 665.
19. C. N. Yarnitzky, N. Klein and O. Cohen, *Talanta*, **40**, (1993), 1937.

20. C. M. N. V. Almeida, R A. S. Lapa, J. L. F. C. Lima, E. A. G. Zagatto and M. C. U. Araujo, *Anal. Chim. Acta*, **407**, (2000), 213.
21. J. F. van Staden and H. du Plessis, *Anal. Commun.*, **34**, (1997), 147.
22. J. F. van Staden and H. du Plessis, *Talanta*, **52**, (2000), 83.
23. G. D. Marshall and J. F. van Staden, *Process Control Qual.*, **3**, (1992), 251.
24. D. McCormack and A. Roach, *Measurement, Statistics and Computation. Analytical Chemistry by Opening Learning.*, (1987), Wiley
25. G. D. Christian, *Analytical Chemistry*, (1994), 5th Ed, John Wiley and Sons.

Chapter 4

On-line dilution and determination of concentrated hydrochloric acid using a sequential injection titration system.

4.1 Introduction

Rapid analysis of concentrated solutions is quite important for process controlling production plants. Pre-dilution of samples is often necessary before performing analysis since the concentration of the samples is too high for direct measurement. Manual dilutions are often tedious, time and reagents consuming and are usually the source of experimental errors in routine analysis. They are also undesirable for toxic samples. Most commercial diluters and robots operate batchwise and the diluted solutions are produced where equilibrium conditions prevail. Until recently, the widely accepted procedure for on-line dilution has been the use of flow injection analysis. This has been used for rapid automated sample dilutions under non-equilibrium conditions [1 - 9]. Some of the procedures used in FIA on-line dilution are as follows: splitting zone, gradient chamber-based zone sampling, cascade systems, merging stream and the use of pre-valve dilution, but the main disadvantage of the flow injection methods is the high reagent consumption. Zone sampling and splitting methods require a source of timing, making the systems more complicated. Gradient chambers have low sampling rates and high reagent consumption.

The concept and methodology of sequential injection analysis [10] have been earlier introduced

and is widely accepted in performing rapid analysis. The SIA manifold is assembled from a pump, a selection valve, a holding coil and a detector. The detector which in this case is the pH electrode sensor does not influence the sample concentration. The SIA technique is simple, fast, automated and precise with the consumption of reagents in micro-quantities. On-line dilution has been carried out through sample dispersion, application of multi syringe flow analysis and single standard calibration [11 - 12]. The on-line dilution was further demonstrated by introducing a dilution conduit for storing concentration gradient of an injected analyte [13]. Most common methods for on-line dilution need a decrease in the sample volume or increasing the length of the flow system tubing.

For this project, a second pump was introduced to effect sample dilution. It operated through two channels, one for the sample and the other for the diluent. Both pumps were fully operated automatically by the computer. The flow rates of both the sample and the diluent streams determine the extent of dilution. The operation of this system is similar to the previous work [14], except that this has the added advantage of on-line dilution. The sample and the diluent are merged within the dilution coil. The stream is then split into waste and the diluted sample was aspirated through port 2 of the selection valve (Figure 4.1A) into the sequential injection titration system. The extent of sample dilution required is achieved by varying the flow rates. A high flow rate causes back-pressure resulting in the disruption of the dilution system manifold.

4.2 Experimental

4.2.1 Apparatus

The dilution system used in the titration is illustrated in Figure 4.1A. It was constructed from two Gilson Minipuls 3 peristaltic Pumps (Villiers-le Bel, France), a 10-port electrically actuated selection valve (Model ECSD10P, Valco Instrumentation, Houston, Texas, USA) and a pH electrode (Hamilton, Switzerland) connected to an Orion Research Process Ionalyzer (Model 901). Data acquisition and device control were achieved by using a PC 30-B interface board (Eagle Electric, Cape Town, South Africa) and an assembled distribution board (MINTEK, Randburg, South Africa). The FlowTEK [15] software package (obtainable from MINTEK) for computer-aided flow analysis was used through out for device control and data acquisition. Tygon tubing was used for the construction of the holding coil (HC) and the reaction coils (RC). The length and diameter of the tubing used are indicated in Figure 4.1A.

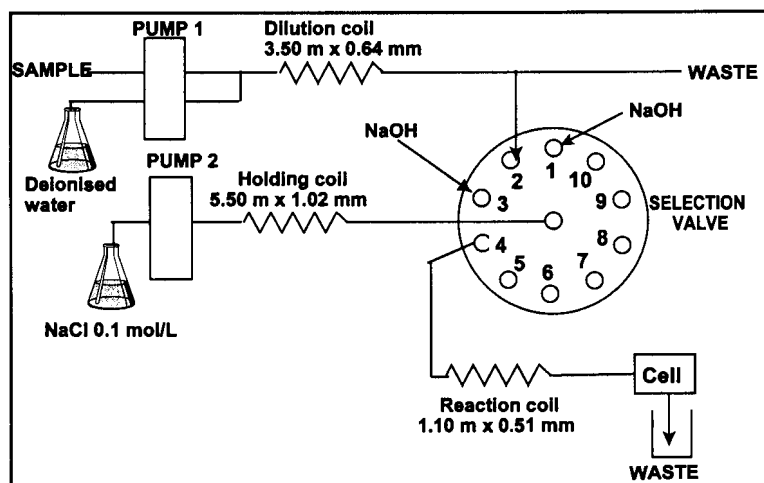


Figure 4.1A Schematic representation of the dilution system coupled to the sequential injection titration system.

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

4.2.2 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.

4.2.2.1 Sodium chloride solution

A 0.1 mol/l sodium chloride used as carrier was prepared by dissolving 11.688 g of dried sodium chloride in 2 l of distilled water.

4.2.2.2 Sodium hydroxide solutions

Sodium hydroxide working solutions were prepared by appropriate dilution of 0.989 mol/l sodium hydroxide stock solution (Titrisol standard solution, Merck) standardized against potassium hydrogen phthalate (Merck).

4.2.2.3 Hydrochloric acid standard solutions

Hydrochloric acid standard solutions were prepared by appropriate dilution of 32 % concentrated

hydrochloric acid. The concentrations of the standard solutions were in the range 5.934 to 8.995 mol/l.

4.2.2.4 Samples

Six samples from a hydrochloric acid production plant were directly analyzed without any sample pretreatment.

4.2.3 Procedure

Figure 4.1B show a schematic diagram of the dilution system, with the device sequence in Table 4.1. Two channels in pump 1 were utilized for the sample and diluent streams which were then mixed in a dilution coil. The whole procedure, from sample injection to data processing and storage was computer controlled via the FlowTEK program. The flow rate of the sample was 0.030 ml/min while for the diluent was 3.5 ml/min. The sample and the diluent were merged within the dilution coil. The sample stream was then split into waste and the diluted sample through port 2 of the selection valve into the SI titration system. The sample was then sandwiched between two sodium hydroxide in the holding coil and propelled through the detector as applied in the previous method.

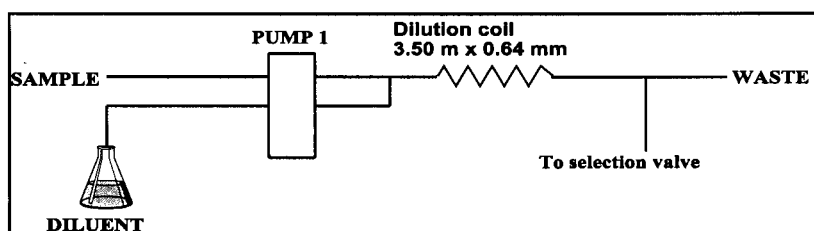


Figure 4.1B Schematic representation of the dilution system.

Table 4.1 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

4.3 Results and Discussion

Two channels in the Gilson minipuls 3 peristaltic pump was employed to merge the sample and the diluent streams which was mixed in the dilution coil. Inner diameters (Figure 4.2), length and the pump speed were studied in order to see how they affect dilution and precision in the dilution system. The inner diameter was kept at 0.64 mm because precision deteriorated as the inner diameter was increased but the peak width was the same (Figure 4.2).

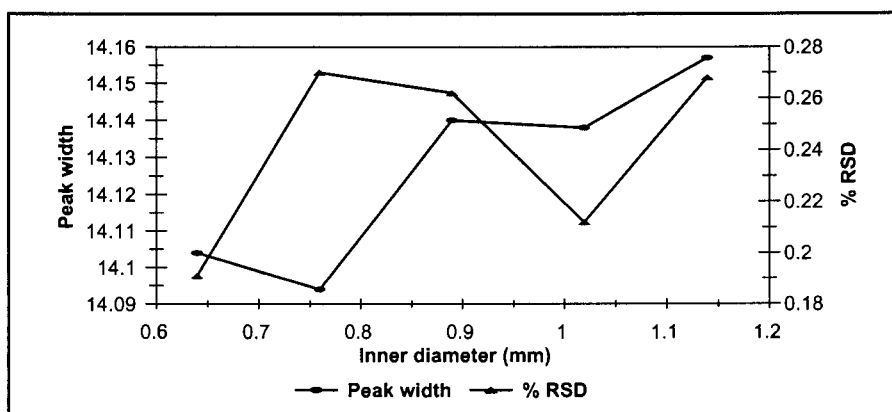


Figure 4.2 Influence of the tube inner diameter on peak width and percentage RSD ([NaOH] = 0.005 mol/l; [HCl] = 7.145 mol/l).

The tube length of the dilution coil was optimised. The optimum length of 3.5 m tubing (Figure 4.3) was used. The peak width decreased as the tube length increased and at shorter tubes because of larger dispersion. The effect of pump speed was evaluated between 10 and 12.5 rpm (Figure 4.4). A speed of 10 rpm was chosen as optimum because it gave by far the lowest percentage RSD of 0.165. The peak width increased with an increase in pump speed because dilution was not good and hence lower speed was preferred. The concentration of 0.005 mol/l of sodium hydroxide was used in the evaluation of the system.

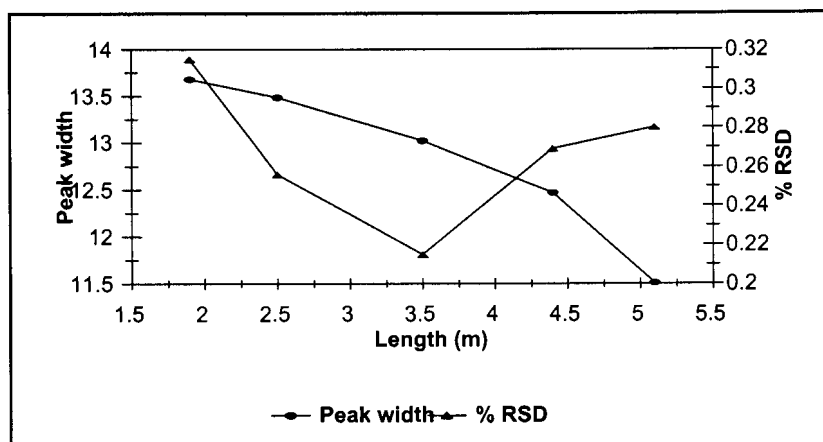


Figure 4.2 Influence of tube length on peak width and percentage RSD ($[\text{NaOH}] = 0.005 \text{ mol/l}$; $[\text{HCl}] = 7.145 \text{ mol/l}$).

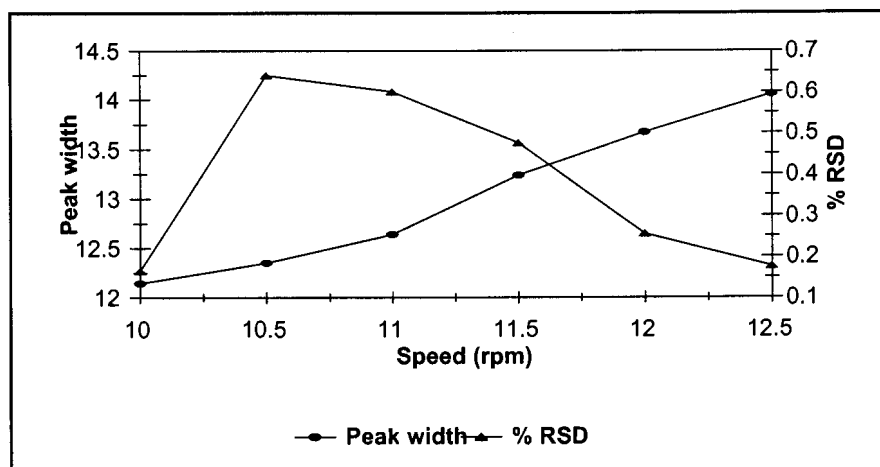


Figure 4.4 Influence of pump speed on peak width and percentage RSD ($[\text{NaOH}] = 0.005 \text{ mol/l}$; $[\text{HCl}] = 7.145 \text{ mol/l}$).

Various dilutions can be made by controlling the flow rate ratio of the diluent to sample. The flow rate of the diluted sample was higher than the one used for the normal titration system, these

resulted in the splitting of the stream to avoid back-pressure. The system was evaluated with regard to linearity, reproducibility and accuracy. The resulting peaks of the system are shown in Figure 4.5.

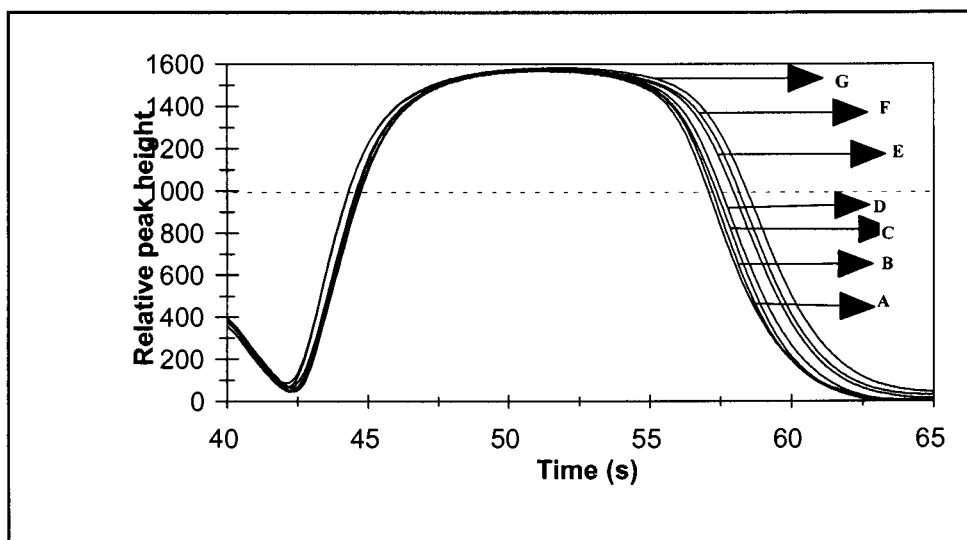


Figure 4.5 SI titration peaks of different concentrations of hydrochloric acid titrated with 0.005 mol/l sodium hydroxide: (A) = 5.934, (B) = 6.566, (C) = 7.145, (D) = 7.579, (E) = 8.062, (F) = 8.495, (G) = 8.995 mol/l.

The accuracy of the proposed dilution system was evaluated by comparing the results obtained with the proposed dilution system with those obtained from a manually performed titration and an automated titration for six samples (Table 4.2). The results shows a percentage RSD of less than 0.4 which is better than for the two standard titrations (Tables 4.2 and 4.3).

Table 4.2 Comparison of results of concentrated hydrochloric acid samples obtained by the proposed SI dilution system with standard manual and automated batch titration methods*.

	SI titration		Manual		Automated	
	(mol/l)	% RSD	(mol/l)	% RSD	(mol/l)	% RSD
Sample 1	6.781	0.286	6.725	1.47	6.749	0.929
Sample 2	6.722	0.26	6.659	2.272	6.664	0.203
Sample 3	6.575	0.189	6.594	0.865	6.6	0.524
Sample 4	6.657	0.324	6.653	0.476	6.673	0.445
Sample 5	6.756	0.277	6.732	0.338	6.737	0.822
Sample 6	6.711	0.143	6.705	0.291	6.696	0.487

*n = 10

Table 4.3 Precision of the proposed SI dilution system.

Standard	% RSD (n = 10)
5.938 mol/l	0.32
6.566 mol/l	0.315
7.145 mol/l	0.316
7.579 mol/l	0.316
8.062 mol/l	0.232
8.497 mol/l	0.252
8.995 mol/l	0.238

The linearity of the SIA system was evaluated for concentrated hydrochloric acid ranging from 5.934 to 8.995 mol/l under optimum running conditions. The relationship obtained between response and concentration was given by the equation $W = 10.405\text{pH} + 2.547$ ($r^2 = 0.9983$)

where W = peak width and these results are obtained from a series of replicative measurements.

4.4 Statistical comparison

The comparison was done between the proposed dilution system and the standard manual and the automated batch titration methods (Table 4.2). The comparison was done in order to establish whether the dilution system can be accepted as giving reliable results. The null hypothesis which assumes that the quantities from two different methods are the same was used in order to check if the results from these methods will agree. The t-test with the multiple samples (paired by differences) was applied to examine whether the methods differed significantly at 95 % confidence level. The null hypothesis $H_0: \zeta = 0$, against the alternative $H_1: \zeta \neq 0$, where ζ is the population paired difference [16, 17]. The test is two tailed, as we are interested in both $\bar{x}_D < 0$ and $\bar{x}_D > 0$ where \bar{x}_D is the mean difference between the methods. The t-data paired test analysis was performed using the formula: $t_{\text{calc}} = |\bar{x}_D| \times \sqrt{n} / s_x$ where s_x is the standard deviation. The results obtained between SI dilution and manual titration was $\bar{x}_D = 0.02223$ and $s_x = 0.03194$ and the results between SI dilution and automated titration was $\bar{x}_D = 0.01383$ with $s_x = 0.03068$. For six determinations, the degrees of freedom was five and at 95 % confidence level $t_{0.05,5} = 2.571$ with the critical t-values being ± 2.571 . When substituting for t_{calc} , it was found to be 1.710 and 1.104 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.

4.5 Conclusions

The dilution system was applied for the on-line determination of concentrated hydrochloric acid.

The peristaltic pump offers constant flow of the sample and diluent. The system is comparable with the manual titration and an automated titration with respect to reproducibility, accuracy, time and speed.

4.6 References

1. G. D. Clark, J. Ruzicka and G. D. Christian., *Anal. Chem.*, **61**, (1989), 1773
2. J. Toei, *Anal. Lett.*, **21(9)**, (1988), 1633
3. K. K. Stewart and A. G. Rosefield, *Anal. Chem.*, **54**, (1982), 2368
4. M. B. Garn, M. Gisin, H. Gross, P. King, W. Schmidt and C. Thommen, *Anal. Chim. Acta.*, **207**, (1988), 225
5. D. A. Whitman and G. D. Christian., *Talanta*, **36**, (1989), 205
6. Y. Israel, A. Lasztity and R. M. Barnes., *Analyst*, **114**, (1989), 1259
7. Y. Israel and R. M. Barnes., *Analyst*, **116**, (1991), 489
8. J. F. van Staden, *Fresenius Z. Anal. Chem.*, **322**, (1985), 36
9. J. F. van Staden, *Fresenius Z. Anal. Chem.*, **328**, (1987), 68
10. J. Ruzicka and G. D. Marshall, *Anal. Chim. Acta.*, **237**, (1990), 329
11. J. F. van Staden and R. E. Taljaard, *Fresenius Z. Anal. Chem.*, **357**, (1997), 577
12. F. Albertus, B. Horskotte. A. Cladera and V. Cerda, *Analyst*, **124**, (1999), 1373
13. A. Baron, M. Guzman, J. Ruzicka and G. D. Christian., *Analyst*, **117**, (1992), 1839.
14. M. G. Mashamba, J. F. van Staden and R. I. Stefan, *S. Afr. J. Chem.*, *in press*.
15. G. D. Marshall and J. F. van Staden, *Process Control Qual.*, **3**, (1992), 251.
16. D. McCormack and A. Roach, *Measurement, Statistics and Computation. Analytical Chemistry by Open Learning*. (1987) Wiley
17. G. D. Christian, *Analytical Chemistry*, (1994), 5th Ed, John Wiley and Sons.

Chapter 5

A potentiometric determination of acetic acid in vinegar using a sequential injection titration system

5.1 Introduction

Acetic acid is corrosive and has numerous industrial applications. It is used, inter alia, in the manufacture of solvents, synthetic fibres and plastics, dyes, pharmaceuticals etc. Acetic acid can severely attack most materials at higher temperatures [1]. It is the principal acid constituent of vinegars (5 % w/v) and volatile acidity in wines [2].

Vinegar is mainly used by consumers for acidification of salads and vegetables and for seasoning meat and fish. The food industry uses vinegar to preserve and season food at the same time [3]. The determination of acetic acid in vinegar has a significance bearing on the health within households, as too much acid is detrimental to human health. Vinegar production is carried out mainly by oxidation of alcohol-containing liquids utilizing an enzyme which is present in the vinegar bacteria (*Acetobacter* sp.) [4]. It can also be prepared by diluting synthetically produced acetic acid. Besides water, alcohol and acetic acid, vinegar consists of secondary constituents that contribute to its aggressive smell, taste and preserving qualities [3].

Several methods have been proposed for the determination of acetic acid in vinegar: for example, the use of gas phase molecular absorption spectrometry [5] and a piezoelectric crystal sensor [6].

All these methods are based on compound volatility and humidity, pressure and temperature needs to be controlled.

Several continuous flow methods have been reported in literature, such as simultaneous automatic potentiometric determination of acidity [7] and a multi commutated unsegmented flow system with potentiometric detection [8] should be mentioned. Batch titrators are usually characterized by low sample throughput and a high implementation cost. The concept of FI titration, introduced in 1977 [9] has since been described in the determination of acetic acid [3, 4, 10 - 12]. The FI titration technique does not offer the robustness needed in process control and has high reagent consumption which makes the method expensive.

A sequential injection titration of weak acid on which peak area was measured instead of peak width was described by Maskula *et al* [13]. Although the sample throughput of SI is less than in FI titration, the main advantage of sequential injection titration is that it has a low reagents' and sample consumption.

A sequential injection titration system for weak acid using a pH electrode as detector and its application to the determination of the concentration of acetic acid in vinegar samples is discussed. The concept is based on the sandwich of a weak acid sample between two strong base zone volumes. The main advantages of the pH electrode detector are that the results are obtained regardless of the sample colour of the materials and the more cost-effective of the pH electrode detector.

5.2 Preparation, properties and utilisation of acetic acid

Acetic acid is a clear, colourless, flammable, water-soluble, very hygroscopic, highly caustic liquid of pungent acidic odour and taste. It is corrosive and very irritating to skin, eyes, nose and lungs. Prolonged contact with skin causes burns. It can severely attack most materials at high temperature upon aeration. Acetic acid is a relatively stable organic compound.

It has such a high resistance to air oxidation that it can be used as solvent in liquid-phase oxidation (for example p-xylene oxidation) and in the acetylation of cellulose with acetic anhydride to give cellulose acetate (acetyl-cellulose) [1]. Ethanoic acid, ethylic acid, methane carboxylic acid and glacial acetic acid are other names of acetic acid.

Acetic acid is one of the most important intermediate and the most frequently used aliphatic carboxylic acid. It is also important as a solvent and as a reagent in the production of rubber, plastics, acetate fibers, pharmaceuticals, dyes and textiles. Especially for human use, acetic acid is produced biologically through two-step oxidation from ethanol by *Acetobacter sp* [4]. Acetic acid could also be synthesized industrially from methanol and carbon monoxide.

Acetic acid is the principal constituent of vinegars and volatile acidity in wines [2]. Vinegar is used for consumption within the households and as food seasoning and preservative in industry. Until recently, vinegar has been used in the weight loss program. Apple vinegar aid in the digestion process as well as the assimilation of nutrients in the body. It is effective in preventing, or at least relieving joint problems.

Wines contain several types of acid, but acetic acid is present in high quantity. This acid is present in all grapes, and therefore in wines. Good acid levels make a wine crisp and refreshing, supporting the after taste. Acidity also helps to preserve a wine. Wines low in acidity are often described as tasting flabby. If present at more than minimal levels, it makes wine unpleasant.

5.3 Experimental

5.3.1 Apparatus

The sequential injection titration system is illustrated in Figure 5.1. It was constructed from a Gilson Minipuls 3 peristaltic Pump (Villiers-le Bel, France), a 10-port electrically actuated selection valve (Model ECSD10P, Valco Instrumentation, Houston, Texas, USA) and a pH electrode (Hamilton, Switzerland) connected to an Orion Research Process Ionalyzer (Model 901). Data acquisition and device control were achieved by using a PC 30-B interface board (Eagle Electric, Cape Town, South Africa) and an assembled distribution board (MINTEK, Randburg, South Africa). The FlowTEK [14] software package (obtainable from MINTEK) for computer-aided flow analysis was used through out for device control and data acquisition. Tygon tubing was used for the construction of the holding coil (HC) and the reaction coils (RC). The length and diameter of the tubing used are indicated in Figure 5.1.

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

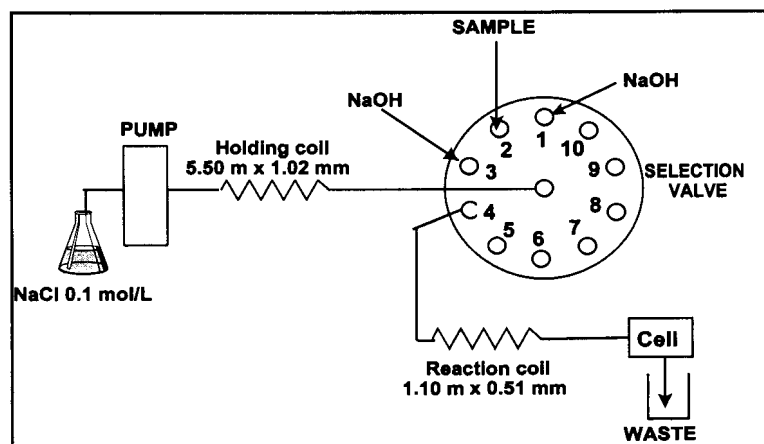


Figure 5.1 Schematic representation of the sequential injection titration system.

5.3.2 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.

5.3.2.1 Sodium chloride solution

A 0.1 mol/l sodium chloride used as carrier was prepared by dissolving 11.688 g of dried sodium chloride in 2 l of distilled water.

5.3.2.2 Sodium hydroxide solutions

Sodium hydroxide working solutions were prepared by appropriate dilution of 0.92 mol/l sodium

hydroxide stock solution (Titrisol standard solution, Merck) standardized against potassium hydrogen phthalate (Merck).

5.3.2.3 Acetic acid standard solutions

Acetic acid standard solutions were prepared by appropriate dilution of 17.643 % glacial acetic acid (Merck) stock solution in the range 1 % to 9 %.

5.3.2.4 Samples

Six vinegar samples were directly analyzed without any sample pretreatment.

5.3.3 Procedure

Figure 5.1 shows a schematic diagram of the system, with the device sequence in Table 5.1. The titration was carried out by aspirating the base zone 1 for 12 s followed by the acid for 6 s and lastly the base zone 2 for 6 s into the holding coil. The zones were propelled through the reaction coil to the detector. The peak widths were measured at a peak height of 1250 as the zones pass the electrode. The time needed to complete one cycle was 130 s and the valve returned to its first position.

Table 5.1 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 CH ₃ COOH sample stream (valve position 2)
15	Reverse		Draw up CH ₃ COOH sample
21	Off		Pump stop
22		NaOH	Select NaOH stream (valve position 3)
23	Reverse		Draw up NaOH solution
29	Off		Pump stop
30		Detector	Pump select detector line (valve position 4)
31	Forward		Pump stack zones to the detector
130	Off	Home	Pump off, return valve to position 1

5.4 Results and Discussion

A potentiometric sequential injection titration system is described for the determination of acetic acid. The determination of this weak acid is based on the original concept of sequential injection titration [15] where the sample is sandwiched between two base zone volumes.

5.4.1 Method 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.

5.4.1.1 Flow rate

A concentration of 2 % sodium hydroxide and 5 % acetic acid were used in the optimization process. The effects of flow rates on peak width and percentage relative standard deviation (RSD) were studied within the range 1.9 and 2.6 ml/min as shown in Figure 5.2. The peak width of the resultant peak decreased with increasing flow rates. The best precision was found at a flow rate of 2.27 ml/min where it deteriorated considerably at higher flow rates because sensitivity was affected. A flow rate of 2.27 ml/min was used in the optimization of the other parameters.

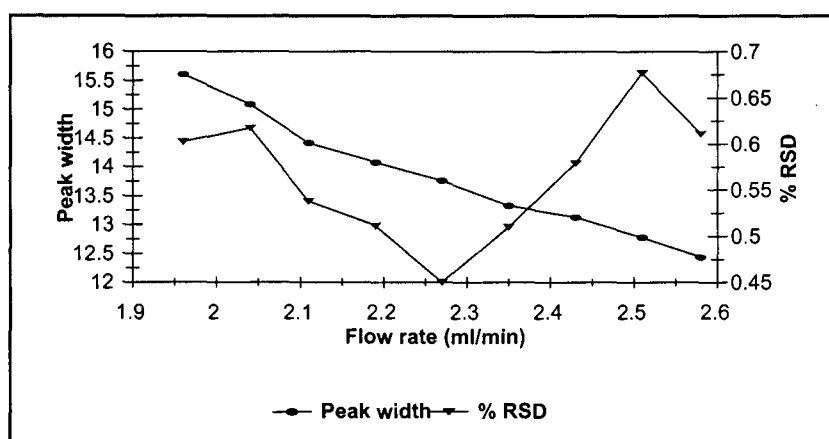


Figure 5.2 Influence of flow rate on peak width and percentage RSD ([NaOH] = 2 %; [CH₃COOH] = 5 %).

5.4.1.2 Base zone volume

The influence of base volume was studied in the range of 200 to 800 μ l (Figure 5.3). The volume of base zone 1 was always twice that of zone 2 to have two peaks of equal heights for

base 1 and base 2 after the dispersion [15]. Precision was not greatly affected at lower volume but deteriorated at higher volumes. A volume of 454 μl was chosen because of lower percentage RSD (Figure 5.3).

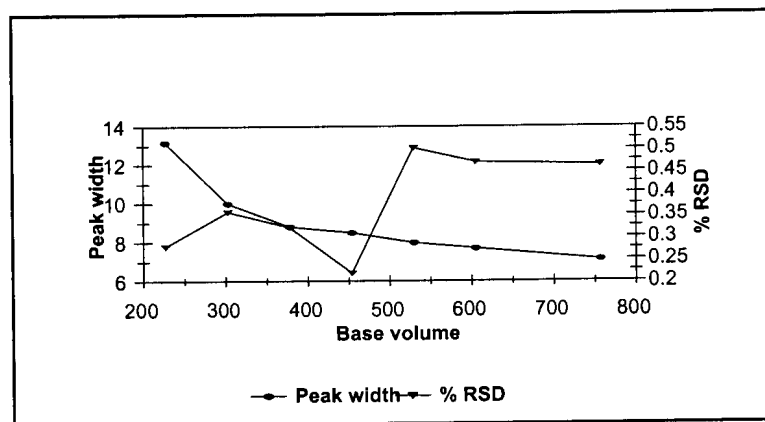


Figure 5.3 Influence of base volume (μl) on peak width and percentage RSD ($[\text{NaOH}] = 2\%$; $[\text{CH}_3\text{COOH}] = 5\%$).

5.4.1.3 Sample volume

Different sample volumes were investigated in the range 150 to 350 μl (Figure 5.4). Peak width increased with increasing sample volume. Precision was not good at lower volume due to low sensitivity but good at higher volumes. A volume of 227 μl was selected showing that larger volume is needed for the weaker acid as compared to the stronger acid.

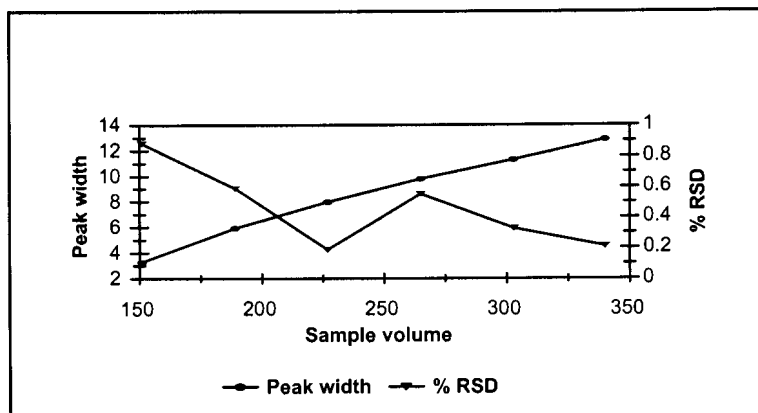


Figure 5.4 Influence of sample volume (μl) on peak width and percentage RSD ($[\text{NaOH}] = 2\%$; $[\text{CH}_3\text{COOH}] = 5\%$).

5.4.1.4 Sodium hydroxide concentration

The linear range was greatly affected by changing the sodium hydroxide concentration. A concentration of 0.4 % sodium hydroxide was used for 0.7 % to 5 % for acetic acid, 1.2 % sodium hydroxide for 1 % to 9 % acetic acid and 2 % sodium hydroxide for 5 % to 13 % acetic acid. A concentration of 1.2 % was used in the evaluation of the method.

5.4.2 Method evaluation

The optimized sequential injection system was evaluated with regard to linearity, accuracy, precision and sample frequency. The samples were analyzed without any pretreatment.

5.4.2.1 Linearity

The sequential injection titration peaks of different acid concentrations are shown in Figure 5.5. The dotted line indicating the height, at which the peak width was measured. The calibration curve of the sequential injection titration system was found in the linear range 1 % to 9 % with $r^2 = 0.99912$ and $W = 15.142 \log C + 12.308$ where W = peak width

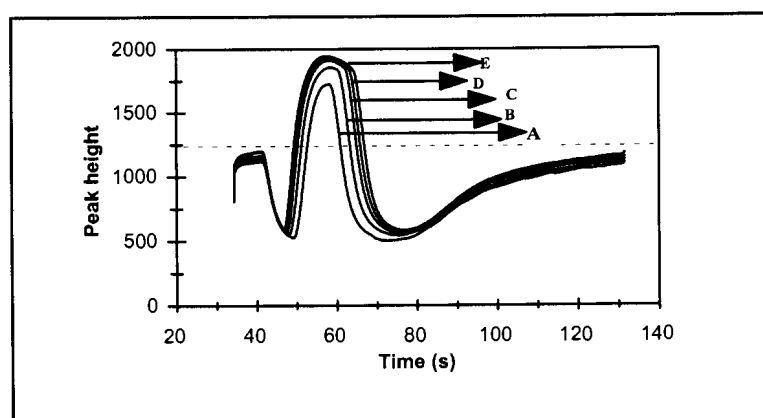


Figure 5.5 SI titration peaks of different concentrations of acetic acid titrated with 1.2 % sodium hydroxide, the peak width measured at 1250 (A = 1 %, B = 3 %, C = 5 %, D = 7 % and E = 9 %)

5.4.2.2 Accuracy

The accuracy of the proposed system was evaluated by comparing the results obtained with the sequential injection titration system with those of the automated titration for vinegar samples. The results given in Table 5.2 revealed good agreement between the sequential injection titration and automated titration method.

Table 5.2 Comparison of results for vinegar samples determined by the SI titration system and automated titration method*.

Sample	SI titration (%)	% RSD	Automated titration (%)	% RSD
White vinegar	4.616	0.27	4.66	0.321
White vinegar	4.934	0.3	4.876	0.353
White vinegar	4.898	0.398	4.858	0.421
Brown vinegar	5.474	0.154	5.452	0.336
White vinegar	5.038	0.236	5.014	0.313
White vinegar	4.948	0.211	4.888	0.436

*n = 10

5.4.2.3 Precision

The reproducibility of the system was evaluated by making ten repetitive determinations of vinegar samples within the linear range of the method. The percentage RSD of less than 0.4 was found as shown in Tables 5.2 and 5.3.

Table 5.3 Precision of the proposed SI titration system

Standard (%)	% RSD (n = 10)
1	0.39
3	0.161
5	0.324
7	0.36
9	0.257

5.4.3.4 Sample frequency

One cycle took 130 s which resulted in the system being able to analyze 28 samples per hour and the system have overall minimum reagent consumption.

5.5 Statistical comparison

The comparison was done between the proposed SI titration system and the standard automated titration method (Table 5.2). The comparison was done to establish whether the SI titration system can be accepted as giving reliable results. The null hypothesis which assumes that the quantities from two different methods are the same was used in order to check if the results from these methods will agree. The t-test with the multiple samples (paired by differences) was applied to examine whether the methods differed significantly at 95 % confidence level. The null hypothesis $H_0: \zeta = 0$, against the alternative $H_1: \zeta \neq 0$, where ζ is the population paired difference [16, 17]. The test is two tailed, as we are interested in both $\bar{x}_D < 0$ and $\bar{x}_D > 0$ where \bar{x}_D is the mean difference of the methods. The t-data paired test analysis was performed using the formula: $t_{\text{calc}} = |\bar{x}_D| \times \sqrt{n} / s_x$ where s_x is the standard deviation. The results obtained between SI titration system automated titration was $\bar{x}_D = 0.0267$ and $s_x = 0.0382$. For six determinations, the degrees of freedom was five and at 95 % confidence level $t_{0.05,5} = 2.571$ with the critical t-values being ± 2.571 . When substituting for t_{calc} , it was found to be 1.712. Since this value lies below the critical t-values, the proposed method can be accepted because the results are comparable at 95 % confidence level.

5.6 Conclusions

The proposed SI titration system gave the best response and precision and it offers the advantages of minimum reagent consumption as compared to automated titrations and flow injection titrations. It is cheap and fully computerized. For the weak acid the only difference is that high sample volume is required as to compared to the strong acid. The method gives good results that are comparable to those of the reference method.

5.7 References

1. DECHEMA Corrosion Handbook: Corrosive agents and their interaction with materials, D. Behrens (ed), DECHEMA Deutsche Gesellschaft Fur Chemisches Apparatewesen, Chemische Technik und Biotechnologie D-6000 Frankfurt am Main, **6** (1990).
2. H. Ebner and H. Folman, *Biotechnology*, XV, H. J. Rehm and G. Reed (ed), Weinheim, (1983).
3. M. Tubino and F. G. Barros, *J. Assoc. Off. Anal. Chem.*, **74**, (1991), 346.
4. T. Becker, R. Kittsteiner-Eberle, T. Luck and H. L. Schmidt, *J. Biotechnology*, **31**, (1993), 267.
5. I. Sanz-Vincente, S. Cabredo and J. Galban, *Mikrochim. Acta*, **134** (2000), 199.
6. J. A. M. Levy, J. L. H. H. Decisneros and D. G. G. Debarreda, *Talanta*, **40**, (1993), 1725.
7. R. A. S. Lapa, J. L. F. C. Lima, R. Perez-Olmos and M. P. Ruiz, *Food Control*, **6**, (1995), 155.
8. C. M. N. V. Almeida, R. A. S. Lapa, J. L. F. C. Lima, E. A. G. Zagatto and M. C. U. Araujo, *Anal. Chim. Acta*, **407**, (2000), 213.
9. J. Ruzicka, E. H. Hansen and H. Mosbaek, *Anal. Chim. Acta*, **92**, (1977), 235.
10. M. D. Capelato, A. M. dos Santos and O. Fatibello-filno, *Anal. Lett.*, **29**, (1996), 711.
11. R. S. Honorato, M. C. U. Araujo, G. Veras, E. A. G. Zagatto, R. A. S. Lapa and J. L. F. C. Lima, *Anal. Sci*, **15**, (1999), 665.
12. P. B. Martelli, B. F. Reis, M. Korn and J. L. F. C. Lima, *Anal. Chim. Acta*, **387**, (1999), 165.
13. S. Maskula, J. Nyman and A. Ivaska, *Talanta*, **52**, (2000), 91.

14. G. D. Marshall and J. F. van Staden, *Process Control Qual.*, **3**, (1992), 251.
15. J. F. van Staden and H. du Plessis, *Anal. Commun.*, **34**, (1997), 147.
16. D. McCormack and A. Roach, *Measurement, Statistics and Computation. Analytical Chemistry by Open Learning*. (1987) Wiley.
17. G. D. Christian, *Analytical Chemistry*, (1994), 5th Ed, John Wiley and Sons.

Chapter 6

Determination of total acidity in soft drinks using potentiometric sequential injection titration analysis

6.1 Introduction

Titration is a very reliable, easily understood and readily applicable analytical tool in routine laboratories and on-line process analysis. The main requirements in process control are speed, high degree of automation and cost effective. Automatic methods of analysis [1-6] usually require complicated ancillary units to facilitate sample introduction, draining and washing of the titration vessel and usually replenishing the titrant delivery.

The concept of the flow injection titration technique has been introduced [7] and has since been applied [8-15]. The method is based on gradient exploitation where the distance between two points of identical amplitude in an analytical signal is proportional to the logarithm of acid concentration. The titrant solution was used as a carrier. The injected sample was mixed with the titrant in gradient chamber before detection. The flow injection titration technique does not offer the robustness needed in process control and has a high reagent consumption which makes the method expensive. The sequential injection titration technique was first introduced in 1997 [16]. This technique is fast, automated and precise with the consumption of reagents in micro-quantities. A sequential injection titration technique using the pH electrode as a detector and its application to the determination of total acidity in soft drinks is described. Soft drinks contain

several acids like for example, citric acid, phosphoric acid, lactic acid, fumaric acid and ascorbic acid. These acids are used as acidulants and they are of considerable importance in determining the sensory quality of soft drinks. For the searched soft drinks, the total acidity is given by the amount of citric acid per 100ml of soft drinks [17]. Five samples of soft drinks were degassed prior to analysis.

6.2 Properties, preparation and utilisation of citric acid

Citric acid is a natural occurring fruit acid. It exists widely in nature, such as in lemon, orange, pineapple, plum, pear and peach and in animal bones, muscles and blood. Citric acid is the most widely used organic acidulant and pH-control agent in foods, beverages, pharmaceuticals and technical applications. Its structure is shown below:

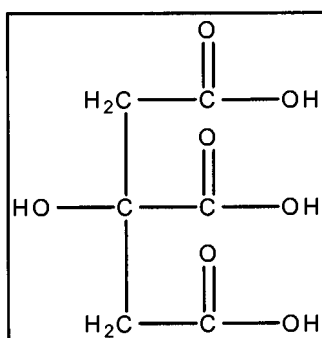


Figure 6.1 Structure of citric acid.

Citric acid monohydrate and anhydrous occur as colourless crystals or a white, crystalline powder. These are odourless substances with strongly acidic taste, slightly deliquescent in moist air, very soluble in water, freely soluble in 96 % ethanol and sparingly soluble in ether. The crystals or powder are non-toxic, have a low reactivity and are chemically stable if stored at

ambient temperatures.

Citric acid is produced by fermentation processes using natural, renewable raw materials such as molasses and other carbohydrates. A large part of citric acid in the world is produced by use of *Aspergillus niger* that is fermented on saccharide materials. The raw materials that can be used in production of citric acid are: pure sugar, starch and sugarcane or beet molasses.

Besides the main use of citric acid in the manufacture of soft drinks, citric acid is used extensively in the processing of a wide variety of foods, in pharmaceutical preparations and for a range of technical and industrial applications. Citric acid has a cleansing and sequestering properties and can be used in detergents, industrial and domestic cleaners. It is also employed as an industrial cleaner to remove rust and scale and for pretreatment of metals prior to coating. In pharmaceutical industries it is included in the formulation for many types of effervescent tablets where it helps to create the bubbling and fizzing effect. Citric acid is also used in the cosmetic industry where it is included in various creams, ointments and shampoos.

Citric acid is directly responsible for the production of energy by means of the Krebs cycle in addition to being essential in several processes such as the metabolism of fatty acids, carbohydrates and certain amino acids.

The main functions of citric acid in soft drinks is to serve as a flavour adjunct, to improve taste, as a pH control agent, for example for gellation control, buffering and preservative enhancement. It is also used as a chelating agent where it improves the action of antioxidants and prevents spoilage of foods such as seafood.

6.3 Experimental

6.3.1 Apparatus

The sequential injection titration system is illustrated in Figure 6.2. It was constructed from a Gilson Minipuls 3 peristaltic Pump (Villiers-le Bel, France), a 10-port electrically actuated selection valve (Model ECSD10P, Valco Instrumentation, Houston, Texas, USA) and a pH electrode (Hamilton, Switzerland) connected to an Orion Research Process Ionalyzer (Model 901). Data acquisition and device control were achieved by using a PC 30-B interface board (Eagle Electric, Cape Town, South Africa) and an assembled distribution board (MINTEK, Randburg, South Africa). The FlowTEK [18] software package (obtainable from MINTEK) for computer-aided flow analysis was used through out for device control and data acquisition. Tygon tubing was used for the construction of the holding coil (HC) and the reaction coils (RC). The length and diameter of the tubing used are indicated in Figure 6.2.

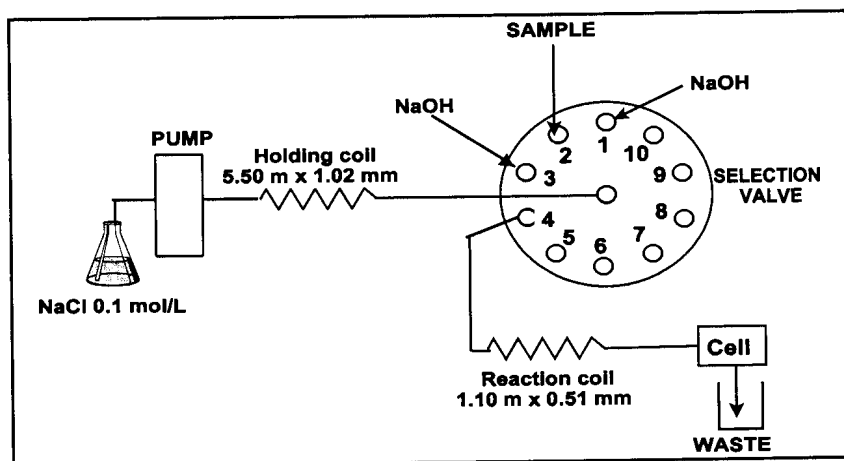


Figure 6.2 Schematic representation of sequential injection titration system.

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

6.3.2 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.

6.3.2.1 Sodium chloride solution

A 0.1 mol/l sodium chloride used as carrier was prepared by dissolving 11.688 g of dried sodium chloride in 2 l of distilled water.

6.3.2.2 Sodium hydroxide solutions

Sodium hydroxide working solutions were prepared by appropriate dilution of 1 % sodium hydroxide stock solution (Titrisol standard solution, Merck) standardized against potassium hydrogen phthalate (Merck).

6.3.2.3 Citric acid standard solutions

Citric acid standard solutions were prepared by appropriate dilution of 5 % citric acid (Merck)

stock solution in the range 0.1 % to 0.6 %.

6.3.2.4 Samples.

Five samples of soft drinks were degassed prior to analysis to remove all dissolved gases so that they do not pass through the titration cell which will result in skewed peaks.

6.3.3 Procedure.

Figure 6.2 shows a schematic diagram of the system, with the device sequence in Table 6.1.

Table 6.1 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
12	Off		Pump stop
13		Sample	Select sample stream (valve position 2)
14	Reverse		Draw up sample
17	Off		Pump stop
18		NaOH	Select NaOH stream (valve position 3)
19	Reverse		Draw up NaOH solution
24.5	Off		Pump stop
25.5		Detector	Pump select detector line (valve position 4)
26.5	Forward		Pump stack zones to the detector
90	Off	Home	Pump off, return valve to position 1

The titration was carried out by aspirating the base zone 1 for 11 s followed by the acid for 3 s and lastly the base zone 2 for 5.5 s into the holding coil. The zones were propelled through the reaction coil to the detector. The peak widths were measured at a peak height as the zones passes the electrode. The time needed to complete one cycle was 90 s and the valve returned to its first position.

6.4 Results and Discussion

A schematic representation of sequential injection titration system used for the determination of total acidity in soft drinks is shown in Figure 6.2. The method employs a pH electrode as a detector and a carrier of 0.01 mol/l sodium chloride was used to adjust the ionic strength.

6.4.1 Method Optimization

The system was developed optimizing flow rate and zone volumes separately and considering the best compromise between sensitivity, reproducibility, sampling rate and low consumption of reagents.

6.4.1.1 Flow rate

The effect of flow rate on peak width and reproducibility was studied on the range 1.6 to 2.6 ml/min as shown in Figure 6.3. A concentration of 0.03 % sodium hydroxide and 0.2 % citric acid were used in the optimization process. Sensitivity decreased with increasing flow rate where 2.2 ml/min was found to be the optimum and was used in optimization of other

parameters.

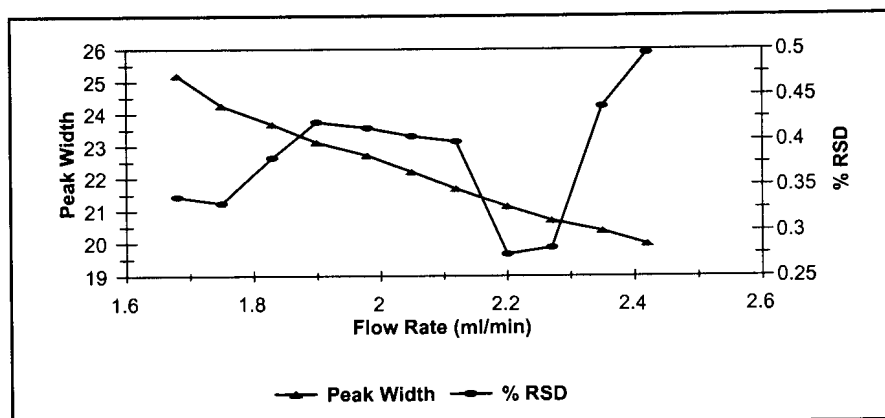


Figure 6.3 Influence of flow rate on peak width and percentage RSD ([NaOH] = 0.03 %; [HOC(CO₂H)(CH₂CO₂H)₂] = 0.2 %).

6.4.1.2 Base zone volume

The influence of base volume was studied in the range of 300 to 650 μ l as shown in Figure 6.4. Peak width decreased as the volume was increased to a point where it was almost constant. A volume of 403 μ l was found to be optimum.

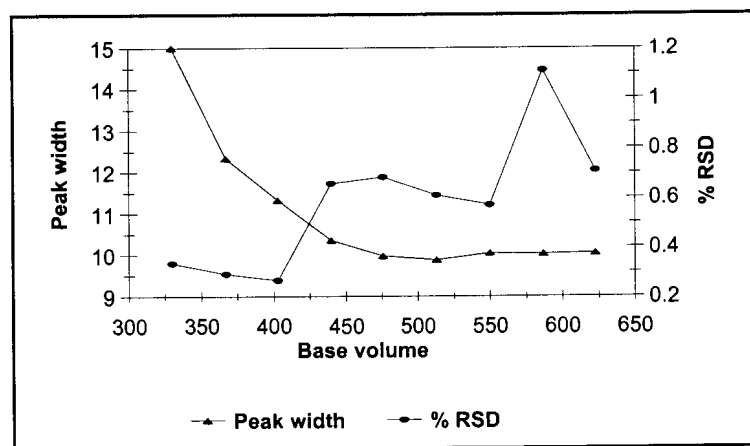


Figure 6.4 Influence of base volume (μ l) on peak width and percentage RSD ([NaOH] = 0.03 %; [HOC(CO₂H)(CH₂CO₂H)₂] = 0.2 %).

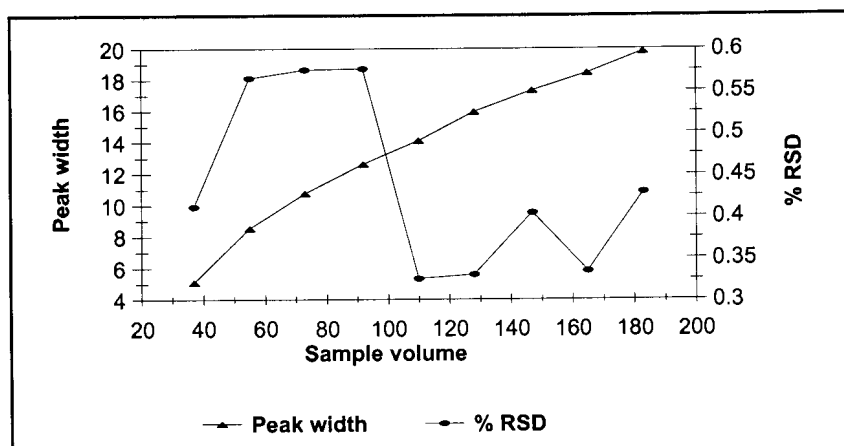


Figure 6.5 Influence of sample volume (μl) on peak width and percentage RSD ($[\text{NaOH}] = 0.03\%$; $[\text{HOC}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})_2] = 0.2\%$).

6.4.1.3 Sample volume

The sample volume was also optimized, studying in the range 30 to 200 μl (Figure 6.5). As the sample volume was increased, peak width also increased because peak width is directly proportional to the acid concentration. The optimum sample volume of 110 μl was found.

6.4.2 Method evaluation

The optimized sequential injection system was evaluated with regard to linearity, accuracy, precision and sample frequency.

6.4.2.1 Linearity

Standard solutions of citric acid at concentrations between 0.1 % and 0.6 % were used to run the calibration curve with a 0.03 % NaOH titrant. The sequential injection titration peaks of different

acid concentrations are shown in Figure 6.6. The dotted line indicate the height at which the peak width were measured. The calibration graph of the sequential injection titration system gave a linear range of 0.1 % to 0.6 % citric acid with the equation: $W = 6.6541 \log C + 17.390$ and $r^2 = 0.99807$ where W = peak width and C = concentration of the sample.

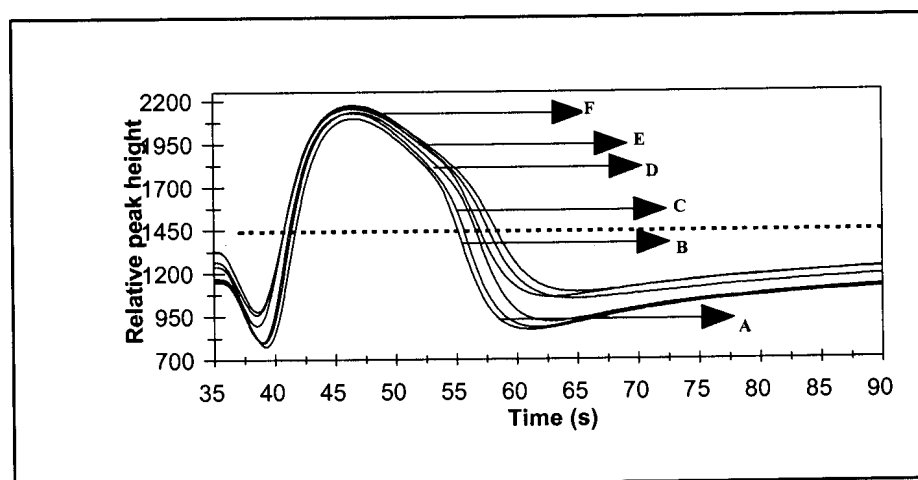


Figure 6.6 SI titration peaks of different concentrations of citric acid titrated with 0.03 % NaOH, the peak width measured at 1450 (A = 0.1 %, B = 0.2 %, C = 0.3 %, D = 0.4 %, E = 0.5 % and F = 0.6 % standards).

6.4.2.2 Accuracy

The accuracy of the proposed system was evaluated by comparing the results obtained with the SI titration system to those of automated and manual titration for the soft drinks samples. The results are given on Table 6.2 which shows good agreement between the methods.

Table 6.2 Comparison of results for soft drinks samples determined by the SI titration system, automated titration and manual titration methods*.

Sample	SI titration (%)	% RSD	Automated titration (%)	Manual titration (%)
S1	0.218	0.401	0.22	0.219
S2	0.229	0.269	0.228	0.233
S3	0.242	0.385	0.24	0.243
S4	0.218	0.256	0.219	0.217
S5	0.209	0.484	0.205	0.206

*n = 10

6.4.2.3 Precision

The reproducibility of the system was evaluated with a run of ten repetitive determinations of samples. The percentage relative standard deviation was found to be 0.5 (Table 6.2)

6.4.2.4 Sample frequency

The method proposed allowed the determination of total acidity in soft drinks samples at a sampling rate of 45 samples per hour. The samples were degassed prior to introduction to the system.

6.5 Statistical comparison

The comparison was done between the proposed SI titration system and the standard manual and the automated batch titration methods (Table 6.2). The comparison was done in order to

establish whether the SI titration system can be accepted as giving reliable results. The null hypothesis which assumes that the quantities from two different methods are the same was used in order to check if the results from these methods will agree. The t-test with the multiple samples (paired by differences) was applied to examine whether the methods differed significantly at 95 % confidence level. The null hypothesis $H_0: \zeta = 0$, against the alternative $H_1: \zeta \neq 0$, where ζ is the population paired difference [19, 20]. The test is two tailed, as we are interested in both $\bar{x}_D < 0$ and $\bar{x}_D > 0$ where \bar{x}_D is the mean difference of the methods. The t-data paired test analysis was performed using the formula: $t_{\text{calc}} = |\bar{x}_D| \times \sqrt{n} / s_x$ where s_x is the standard deviation. The results obtained between SI and automated titration was $\bar{x}_D = 0.0008$ and $s_x = 0.00239$ and the results between SI dilution and manual titration was $\bar{x}_D = -0.0004$ with $s_x = 0.00269$. For 5 determinations, the degrees of freedom was four and at 95 % confidence level $t_{0.05,5} = 2.776$ with the critical t-values being ± 2.776 . When substituting for t_{calc} , it was found to be 0.748 and 0.343 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.

6.6 Conclusions

The potentiometric SI titration system described provides a fast, simple, reliable, inexpensive and sensitive method for the determination of total acidity in soft drinks. The method has a sample frequency of 45 samples per hour with a linear range of 0.1 and 0.6 %. It is easy to use, fully computerized, and gives the results that are comparable to both automated batch titration and manual titration.

6.7 References

1. P. Pillay, D. E. Barnes and J. F. van Staden, *Anal. Chim. Acta*, **440**, (2000), 45.
2. R. Hoogendijk, *Anal. Chim. Acta*, **378**, (1999), 211.
3. J. I. Partanen and P. M. Juusola, *Fluid Phase Equilibria*, **173**, (2000), 135.
4. R. A. S. Lapa, J. L. F. C. Lima, R. Perez-Olmos and M. P. Ruiz, *Food Control*, **6**, (1995), 155.
5. C. De Caro, *GIT Laboratory Journal*, **3**, (2000), 160.
6. R. S. Honorato, M. C. U. Araujo, R. A. C. Lima, E. A. G. Zagatto, R. A. S. Lapa, and J. L. F. C. Lima *Anal. Chim. Acta*, **396**, (1999), 91.
7. J. Ruzicka, E. H. Hansen and H. Mosbaek, *Anal. Chim. Acta*, **92**, (1977), 235.
8. M. D. Capelato, A. M. dos Santos and O. Fatibello-filno, *Anal. Lett.*, **29**, (1996), 711.
9. K. Grudpan, P. Sritharathikhun and J. Jalamunee, *Anal. Chim. Acta*, **363**, (1998), 199.
10. R. H. Taylor, J. Ruzicka and G. D. Christian, *Talanta*, **39**, (1992), 285.
11. P. B. Martelli, B. F. Reis, M. Korn and J. L. F. C. Lima, *Anal. Chim. Acta*, **387**, (1999), 165.
12. J. F. van Staden, *Water SA*, **12**, (1986), 93.
13. J. Toei, *Fresenius' Z. Anal. Chem.*, **330**, (1988), 484.
14. Z. Feher, I. Kolbe and E. Pungor, *Analyst.*, **116**, (1991), 483.
15. N. Ishibashi and T. Imato, *Fresenius' Z. Anal. Chem.*, **323**, (1986), 244.
16. J. F. van Staden and H. du Plessis, *Anal. Commun.*, **34**, (1997), 147.
17. A. H. Varnam and J. P. Sutherland, *Beverages: Technology, Chemistry and Microbiology*, **2**, (1994), Chapman and Hall.
18. G. D. Marshall and J. F. van Staden, *Process Control Qual.*, **3**, (1992), 251.
19. G. D. Christian, *Analytical Chemistry*, (1994) 5th Ed, John Wiley and Sons.
20. D. McCormack and A. Roach, *Measurement, Statistics and Computation. Analytical Chemistry by Open Learning*. (1987) Wiley.

Chapter 7

7.1 Conclusions

There is an increase demand for rapid analysis and miniaturization in industrial and process analytical control. SIA is a technique that has a tremendous potential for on-line processes measurements and in the monitoring of the environment. The development of this technique was aimed at providing industries with reliable, precise and cost-effective instrumentation of performing analysis.

The importance of this work was to develop a process analyser that is capable of on-line determination and dilution which is simple and reliable. The system must also have a high sample throughput with minimum reagent and sample consumption. Sequential injection titration was introduced with the aim of meeting the objectives mentioned above. The method confirmed its feasibility for use in process analysis because it is fully computerised with minimum reagent and sample consumption and good sample frequency although high speed flow injection titration has much higher sample frequency. Both FI titration and SI titration are robust, the difference is that FI systems require higher reagent consumption.

The use of electrochemical detectors has been used in flow injection titration, and now it was important to evaluate their capability in a sequential injection titration system. The importance of using this detector is because of its simplicity, cost-effective and reliability in flow systems. This was applied in the determination of hydrochloric acid for environmental purposes, on-line dilution in production plants, vinegar from food industries and total acidity from the beverage

industries. Quality of food and beverages as well as the quality of environment has a great impact on human health. Unlike indicators which may influence sample concentration, pH electrodes are renewed by on-line polishing with the carrier which on this case was 0.1 mol/l sodium chloride, hence they are suitable for use in flow systems. The proposed method satisfies the requirements needed for process analyser. The system is fully computerised, inexpensive, reliable with minimum reagent or sample consumption and good sample frequency.

The best response and peak shapes as well as precision were obtained with the proposed system. The linear range can easily be adjusted to suit the specific need by just changing the titrant concentration. However the manifold doesn't need to be changed. This system is also useful for acids of higher concentrations by titration with on-line dilution procedure. In industries the analyte concentrations are very high and they need to be pre-diluted before analysis.



APPENDIX

APPENDIX A

Publications and Presentations

Publications

1. On-line determination of hydrochloric acid in process effluent streams by potentiometric sequential injection acid-base titration
M. G. Mashamba, J. F. van Staden and R. I. Stefan
S. Afr. J. Chem., In press.
2. On-line dilution and determination of concentrated hydrochloric acid using a sequential injection titration system.
M. G. Mashamba, J. F. van Staden and R. I. Stefan
Submitted.
3. A potentiometric determination of acetic acid in vinegar using a sequential injection titration system
M. G. Mashamba, J. F. van Staden and R. I. Stefan
Submitted.
4. Determination of total acidity in soft drinks using potentiometric sequential injection titration analysis
M. G. Mashamba, J. F. van Staden and R. I. Stefan
Submitted.

Presentations

1. On-line determination of hydrochloric acid in process effluent streams by potentiometric sequential injection acid-base titration.

M. G. Mashamba, J. F. van Staden and R. I. Stefan

Instrumental Methods of Analysis 2001, University of Ioannina, Greece, 5 - 8

September 2001

2. On-line dilution and determination of concentrated hydrochloric acid using an SI titration system.

M. G. Mashamba, J. F. van Staden and R. I. Stefan

11th International conference on flow injection analysis, including related techniques (ICFA 2001) Chiang Mai, Thailand, 16 - 20 December 2001

3. A potentiometric determination of acetic acid in vinegar using a sequential injection titration system

M. G. Mashamba, J. F. van Staden and R. I. Stefan

11th International conference on flow injection analysis, including related techniques (ICFA 2001) Chiang Mai, Thailand, 16 - 20 December 2001

4. Determination of total acidity in soft drinks using potentiometric sequential injection titration analysis

M. G. Mashamba, J. F. van Staden and R. I. Stefan

11th International conference on flow injection analysis, including related techniques (ICFA 2001) Chiang Mai, Thailand, 16 - 20 December 2001

ADDENDUM

Method construction

Automation of laboratory processes is of utmost importance in analytical chemistry. For this reason all experimental work done was fully or partially run by a computer. Microprocessors are the controlling key feature for device control and data acquisition. Sequential injection analysis depend on precisely timed operations which take place in a definite and well preprogrammed interconnected sequence. These programming was done using the FlowTEK [1,2] program, developed by Marshall [3].

To explain the use of FlowTEK program as it was used in the experimental work for this project, experimental setup for the on-line determination of hydrochloric acid in process effluent streams by potentiometric sequential injection acid-base titration (Chapter 3) was chosen. The analytical cycle used in the determination consisted of the following operations: the aspiration of first base, followed by the acid sample and lastly by the second base into the holding coil. These was later propelled towards the detector after passing through the reaction coil. Following are the steps taken for the setup of the FlowTEK program before use in the experimental work.

A1. Setup of the FlowTEK program for device control and data collection

A1.1 Detector

For all the analysis carried out, the Hamilton pH electrode connected to an Orion Research Microprocessor Ionalyzer was used. The computer is switched on, and the main menu appears on the screen. Dataverwerker is chosen. This leads to a submenu and FlowTek 1.1 is then chosen. The FlowTek page then appears and upon pressing return three times, the FlowTek main page appears. A method can be established by using the words highlighted by the first letter. **S** from **Setup** is chosen. This gives a submenu with different options. **D** for **Detector** is keyed in. The questions and demands which follow must be answered in the following way:

Enter number of detectors	1
Enter signal transformation for detector 1	I
Enter analog input point for detector 1 (1 - 4)	1 (this indicate the position where the detector is coupled to the distribution box)

In the distribution box (PC-30 board), the baseline can be set by adjusting the relevant screw. Direct conversion of the signal could be monitored by using the hotkey F4.

A1.2 Pump and Selection valve

The operation of the pump and selection valve were managed by making use of a **Method**. The method was constructed in the following way:

From the main menu select **Method (M)**. First the devices used in the construction of the method must be identified. From the **Method** menu select **Type device (T)** with the series of options:

Enter number of devices	2 (the pump and selection valve)
Enter type device 1	GP (Gilson Pump)
Enter digital output point for GP	1 (indicates the position of connection of GP on distribution box)
Enter type device 2	SV (Selection valve)
Enter digital output point for SV	3

The experiment time has to be specified by selecting **Expt time (E)** in the **Method** menu and answer the questions to follow: for example

Enter time to start data collection	30
Enter experiment time	120

The screen is now divided into two panels, each containing a straight line in the middle of the panel. The position of these lines represent the 'OFF' position of each device. Programming of

each device are now allowed. The **Num Lock** key is activated and Insert or delete option can be now be used. The actions of the devices can be specified by using the arrow keys which moves the cursor from one device to another. The actions of the Gilson pump are specified as follows:

From the **Method** menu select **Insert (I)** and answer the questions.

Enter device number	1
Enter event (F R O)	
Reverse	R
Off	O
Forward	F

To delete any existing event, the option **Delete (D)** on the **Method** menu must be used. The time of the event needed to be deleted must be typed in when asked for. The procedure to delete an event is the same as the procedure used to insert an event. For the selection valve, the **Insert** option is selected from the **Method** and answer the questions to follow:

Enter device number	2
Enter event (A H)	
Advance	A
Home	H

Various events were inserted to fulfill the requirements of the experiment. After the construction

of a method, the option the **File (F)** on the **Method** menu is used to **Save (S)** the method under an appropriate name. For the hydrochloric acid determination, the **File** on the **Method** menu was selected and the questions were answered in the following way:

Save, Retrieve or Erase (S R E): S
 Enter method file name: C:\FlowTek\mulalo\HCl.met (.met indicating a method file)

The method is now finished and the screen should look like the one given in Figure A.1.

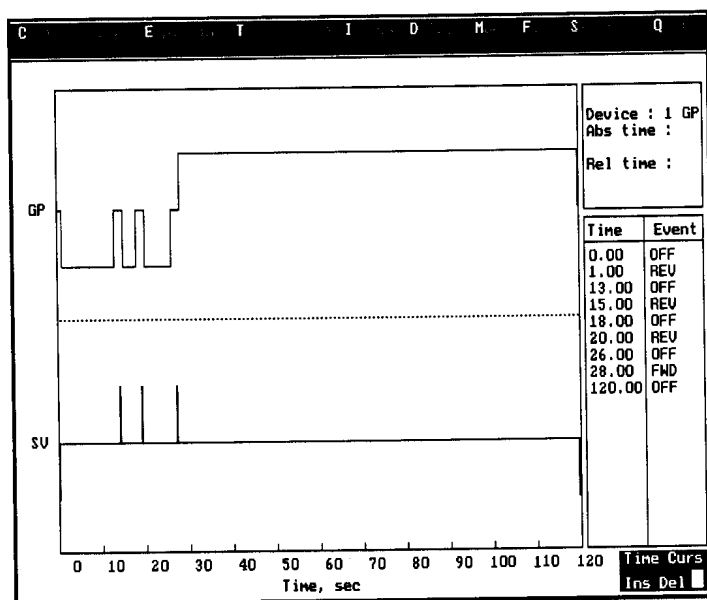


Figure A.1. Schematic representation of the Flow/TEK method screen.

The method constructed can be applied by exiting the menu until to the very first main menu and choose the **Once (O)** option to initiate a single run. The device descriptions can be viewed under the notepad menu (Figure A.2.)

N H R M P Q		Detector						
		1	2	3	4			
Board : PC30-B	Experiment time : 120.0	A/D channel	1					
Zoom min time : 0.0	Zoom max time : 120.0	Transformation	Inverse					
Start acquisition : 28.0	I/O port for GP : 1	Auto Zero	None					
I/O port for SU : 3	Save profile : Yes	AZ time	0.0					
Abridged profile : Yes	Regression on Height	AZ offset	0.000					
Detector displ : Paged	Inject mode : Auto	Min Integ Lim	28.0					
Startup : (0)	Rescale Y-axis : Auto	Max Integ Lim	120.0					
		Width Height	0.000					
		Peak Time	@ Pk max					
		Path : c:\flowtek\MULALO\						
		Main Procedure file : CALIB.PDR						
		Method file : HCL.MET						
		Reduced data file : HCL.RED						
		Experiment Profile Root : HCL						
		Calibration file : DEFAULT.CAL						
F1 : Displ Analog input	F2 : Displ Digital input	Name	CP	CS	CV	AP	GP	IU
F3 : 0000000000 (0)	F4 : 0000000000 (0)	Action	PICK	PICK	IN	FWD	FWD	INJ
F5 : 0000000000 (0)	F6 : 0000000000 (0)		DISP	DISP	OUT	REV	REV	LOAD
F7 : 0000000000 (0)	F8 : 0000000000 (0)	Hotkey	STOP	STOP		OFF	OFF	
F9 : 0000000000 (0)	F10 : Directory		P	P	1	F	F	1
			D	D	0	R	R	L
			T	T	0	0	0	
		Output	01 (1)	01 (1)	1 (1)	01 (1)	10 (2)	01 (1)
			10 (2)	10 (2)	0 (0)	10 (2)	11 (3)	10 (2)
			00 (0)	00 (0)		00 (0)	00 (0)	
		Pulse	0.00	0.00	0.00	0.00	0.00	0.00

Figure A.2. Schematic representation of the FlowTEK notepad screen (page 1 for device descriptions).

The letter N must be typed to view the second page of the device configurations (Figure A.3).

N H R M P Q		Detector						
		1	2	3	4			
Board : PC30-B	Experiment time : 120.0	A/D channel	1					
Zoom min time : 0.0	Zoom max time : 120.0	Transformation	Inverse					
Start acquisition : 28.0	I/O port for GP : 1	Auto Zero	None					
I/O port for SU : 3	Save profile : Yes	AZ time	0.0					
Abridged profile : Yes	Regression on Height	AZ offset	0.000					
Detector displ : Paged	Inject mode : Auto	Min Integ Lim	28.0					
Startup : (0)	Rescale Y-axis : Auto	Max Integ Lim	120.0					
		Width Height	0.000					
		Peak Time	@ Pk max					
		Path : c:\flowtek\MULALO\						
		Main Procedure file : CALIB.PDR						
		Method file : HCL.MET						
		Reduced data file : HCL.RED						
		Experiment Profile Root : HCL						
		Calibration file : DEFAULT.CAL						
F1 : Displ Analog input	F2 : Displ Digital input	Name	SU	SW	SP	0	0	0
F3 : 0000000000 (0)	F4 : 0000000000 (0)	Action	ADV	TRUE	FWD			
F5 : 0000000000 (0)	F6 : 0000000000 (0)		HOME	FALSE	REV			
F7 : 0000000000 (0)	F8 : 0000000000 (0)	Hotkey	A	T	OFF			
F9 : 0000000000 (0)	F10 : Directory		H	F				
					0			
		Output	10 (2)	1 (1)	10 (2)			
			01 (1)	0 (0)	01 (1)			
			00 (0)		00 (0)			
		Pulse	0.30	0.00	0.00	0.00	0.00	0.00

Figure A.3. Schematic representation of the FlowTEK notepad screen (page 2 for device descriptions).

A.2 References

1. G. D. Marshall, *Analytical Instrumentation*, **20(1)**, (1992), 79
2. FlowTEK Reference Manual, *Device Control and Data Acquisition software*, ver 1.1
Mintek, 1993
3. G. D. Marshall, *Sequential-Injection Analysis*, PhD-Thesis, University of Pretoria, 1994