An automatic titrator based on a multicommutated unsegmented flow system: Its application to acid–base titrations

ARTICLE *in* ANALYTICA CHIMICA ACTA · FEBRUARY 2000

Impact Factor: 4.51 · DOI: 10.1016/S0003-2670(99)00826-0

ELSEVIER

Analytica Chimica Acta 407 (2000) 213–223

ANALYTICA CHIMICA ACTA

www.elsevier.com/locate/aca

An automatic titrator based on a multicommutated unsegmented flow system Its application to acid–base titrations

Cristina M.N.V. Almeida [a], Rui A.S. Lapa [a,*], José L.F.C. Lima [a], Elias A.G. Zagatto [b], M.C.U. Araújo [c]

[a] *CEQUP/Departamento de Química-Física, Faculdade de Farmácia UP, Rua Aníbal Cunha, 164, 4050 Porto, Portugal*
[b] *Centro de Energia Nuclear na Agricultura, USP Av. Centenário, Piracicaba, Brazil*
[c] *Laboratório de Automação em Química Analítica, Univ. Federal da Paraíba, João Pessoa, Brazil*

Received 15 July 1999; received in revised form 22 October 1999; accepted 23 October 1999

Abstract

A continuous flow methodology to perform acid–base titrations is described. The titrations are carried out on a multicommutated flow system which simulates batch titration procedures. The titration strategy is based on sequential insertion of increasing titrant and decreasing titrand volumes in a reactor, thus accomplishing complete titration curves. The assessment of the titration end point is similar to that of conventional batch procedures. The theoretical model for the determination of titrand concentration without requiring any calibration process is presented and discussed. The present system was evaluated in vinegar acidity determinations and provided an accuracy better than 3% with a good repeatability (relative standard deviation (RSD) = 2.5%; $n = 10$) and reproducibility (RSD < 5%). The titration accuracy is time-dependent and has been tested in the 2–10 min range.

Keywords: Multicommutated flow system; Titration; Acidity; Vinegar; Potentiometry

1. Introduction

The selection of either direct or titration analysis for determining chemical species depends upon several factors such as precision, sampling rate and instrumentation available, which are usually more favourable for direct analysis. Nevertheless, the lack of selectivity of detection systems and/or non-existence of standards with the same composition as the samples render titration sometimes the only analytical procedure capable of performing some determinations accurately.

To overcome the difficulties usually associated with manual batch titrations, such as time-consuming procedures, several automatic systems have been proposed. Hence, batch titration automatic systems were implemented [1,2], in which despite the automation of some titration steps, the work of an operator for washing the titrator vessel before each determination is still required. In other works, the titrations were performed by using a fully automatic apparatus [3].

Aiming at the minimisation of the disadvantages of automatic batch titration, such as complexity and

* Corresponding author. Fax: +351-2-207-8967.
E-mail address: laparuas@ff.up.pt (R.A.S. Lapa).

0003-2670/00/$ – see front matter
PII: S0003-2670(99)00826-0

expensive equipment, several authors have proposed continuous flow systems. Titrations hereby performed present a stage at which titrant and sample concentrations are at the stoichiometric ratio of the reaction. This stage is usually found when the flow of one of the solutions (titrand or titrant) is kept stable and the other is varied linearly [4,5], or by exploitation of the linear concentration gradient of titrant generated by an external gradient chamber [6].

The flow injection systems gave rise to a new titration procedure based on gradient exploitation where the distance (considered as a period of time) between two points of identical amplitude in the same analytical signal was directly proportional to the logarithm of the concentration [7,8]. Hence, several systems have been proposed and developed, like triangle-programmed flow titrations [9], linear pH-buffering single point titrations [10] and coulometric flow injection analysis [11]. The application of automatic burettes for the insertion of different volumes of titrant in a continuous sample flow enabled to attain analytical signals that match the profile of the titration curve [12].

One particular feature of the existing flow titration systems is that a calibration step is required. However, the lack of adequated standard samples for chemical determinations may be a serious limitation.

Strategies based on concentration gradients with a single standard calibration have also been presented [13]. The concentration of one of the solutions (titrand or titrant) is kept at its steady state throughout the whole process by pumping it continuously. The other is injected and its concentration is determined by the gradient calibration technique.

Other works refer to flow titration based on unsegmented [14] or segmented [15] multicommutated flow systems using a binary search strategy for the end-point determination. Although these titrations do not require any calibration, they can only be applied to systems in which an indicator (or other reference solution) can be used by the binary searching algorithm to decide the next step in the searching process.

In this work, a new titration strategy based on the sequential insertion in a reactor (mixing chamber) of increasing volumes of titrant and decreasing volumes of titrand is presented, the inserted volumes being determined by the valve commutation times. This system enables to attain complete titration curves similar to those of batch titration systems. The software developed is able to control every step of the titration procedure, perform data acquisition and processing. The titration end-point was determined by the second derivative method as in batch titration systems. The theoretical model used was tried out and proved to be suitable for the description of the analytical process. The flow system proposed allows to simulate batch titration procedures without requiring a calibration step. The automatic flow titrator developed was tested for acidity determination in vinegar samples.

2. Theoretical aspects

2.1. Titration strategy

The strategy used is based on the sequential insertion in a reactor (a mixing chamber) of increasing volumes of titrant and decreasing ones of titrand, the inserted volumes being determined by the valve commutation times, to attain complete titration curves. Using this strategy, and considering that the flow-rate is constant, the variable volume can be obtained from the time values.

The titrant valve (V) presents two inlets, one (a) for the titrand (S) and another (b) for the titrant (T) and one outlet (c) that is the same for both leading to the reactor (R) (Fig. 1A).

The strategy used in this titration procedure (Fig. 1) can be described as follows (Fig. 1B).

First, the channel (a) is opened and the filling up of the reactor with titrand takes place (Step 1). Throughout titration procedures, increasing volumes (or times) of titrant and decreasing ones of titrand are inserted in the reactor one after the other, the total volume ($VT = V_{titrand} + V_{titrant}$) or total time ($TT = T_{titrand} + T_{titrant}$) at the end of each cycle being kept the same. The former titrant volume is the same or higher than the lowest volume accurately inserted through the valve (minimum volume). The titrand volumes correspond to the remainder left after subtracting the titrant volume to the total volume (VT), and are thus lower and lower throughout titration.

Once the titration is started, the first titrant volume (Vt_1) is inserted into the reactor, which causes a titrand concentration reduction at the reactor (Step 2).

The next step (Step 3) corresponds to the insertion of a titrand volume (Vs_1, equal to $VT - Vt_1$), thus

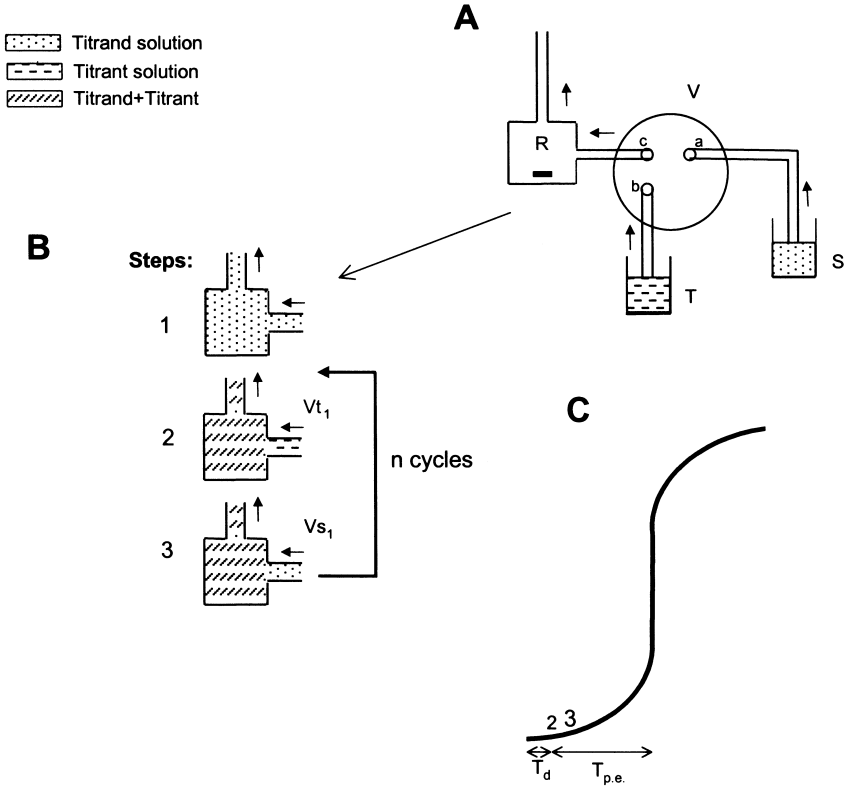

Fig. 1. Schematic representation of the titration strategy. (A) V: titration valve; S: titrand solution; T: titrant solution; R: reactor (mixing chamber); (a) titrand inlet; (b) titrant inlet; (c) outlet channel for both solutions (titrand and titrant). (B) Titration steps, Vt_1: titrant volume (t_1 corresponds to the first titrant volume); Vs_1: titrand volume (s_1 corresponds to the first titrand volume). (C) Plot of a simulated titration curve, t_d: detector reaching time; $T_{p.e.}$: time spent until end-point titration time.

promoting an increase in the titrand concentration in the reactor that is usually smaller than the expected reduction due to the insertion of titrant. The first cycle is hereby ended.

This procedure is performed repeatedly (n cycles) until the titration is complete. During the titration, the titrant volumes inserted in the reactor are higher and higher (by a fixed increment) and the titrand ones lower and lower.

The data attained (Fig. 1C) from the titration process is stored in a local file for data processing, namely, end-point calculation. The titration end-point may be assessed using the second derivative method and it corresponds to the titration time ($T_{p.e.}$) with zero derivative. From the titration times obtained, the detector reaching times (t_d, which correspond to the time necessary for the sample to reach the detector) are deduced.

3. Model used

As already referred to, it was assumed that the reactor (mixing chamber) is initially full of titrand. The variation (reduction) of its concentration during the insertion of titrant (Fig. 1B, Step 2) can be expressed by [18]

$$\mathrm{Ca}(t_x) = \left(-\frac{\mathrm{C}^0\mathrm{t}}{n}\right) + \left(\frac{\mathrm{C}^0\mathrm{t}}{n} + \mathrm{Ca}(t_{y1})\right) \times \exp\left[-\frac{F}{V}(t_1 - t_0)\right] \quad (1)$$

where $\mathrm{Ca}(t_x)$ is the variation of the titrand concentration (mol/l) in the mixing chamber while the titrant is being inserted; $\mathrm{C}^0\mathrm{t}$, the initial concentration (mol/l) of titrant; $\mathrm{Ca}(t_{y1})$, the titrand concentration (mol/l) in the mixing chamber before the insertion of titrant (for

$t = 0$, it is the same as the initial titrand concentration); F, the flow rate (l/s); V, the chamber volume (l); $(t_1 - t_0)$, the time (s) for titrant insertion into the chamber and n, the stoichiometric coefficient of the reaction (titrand/titrant).

The variation (increase) of titrand concentration over the insertion of titrand into the mixing chamber (Fig. 1B, Step 3) can be expressed by [18]

$$\mathrm{Ca}(\mathrm{t}_y) = \mathrm{C}^0\mathrm{a} - (\mathrm{C}^0\mathrm{a} - \mathrm{Ca}(\mathrm{t}_{x1})) \times \exp\left[-\frac{F}{V}(t_2 - t_1)\right] \quad (2)$$

where $\mathrm{Ca}(\mathrm{t}_y)$ is the variation of titrand concentration (mol/l) in the mixing chamber throughout titrand insertion; $\mathrm{C}^0\mathrm{a}$, the initial concentration (mol/l) of titrand; $\mathrm{Ca}(\mathrm{t}_{x1})$, titrand concentration in the mixing chamber after the insertion of titrant (just before the insertion of titrand) and $(t_2 - t_1)$, the time of titrand insertion into the mixing chamber.

Throughout the titration procedure, there is a successive reduction of titrand concentration (though this increased slightly while the titrand was being inserted) in the mixing chamber until the end point is reached. Afterwards, there is an excess of titrant until the titration is complete.

The determination of the theoretical end point time for each titrand concentration is based on Eq. (1) (during the insertion of titrant) and Eq. (2) (during the insertion of titrand), and corresponds to the titration time spent until the titrand excess switches to titrant excess. The variation of the theoretical end-point times with titrand concentration is presented in Fig. 2A.

There is the possibility that an excess of titrant that is consumed by the next insertion of titrand occurs briefly. The theoretical end-point time will thus correspond to the titration time when a constant excess of titrant is attained.

The determination of sample concentration is carried out by an iterative procedure that, based on the Eqs. (1) and (2) of the theoretical model, estimates the sample concentration whose theoretical end-point time corresponds to the experimental value. Therefore, the necessary subroutine allowing the determination of titrand concentration was implemented. This subroutine determines the theoretical end-point titration times corresponding to a simulated concentration interval. After each assessment, the time obtained and the experimental one are compared. Every time this value found is lower than the experimental one, the system moves on to the next concentration (for the assessment of the new theoretical end-point titration time). Only when the time assessed matches the experimental value, the titrand concentration and theoretical one match as well.

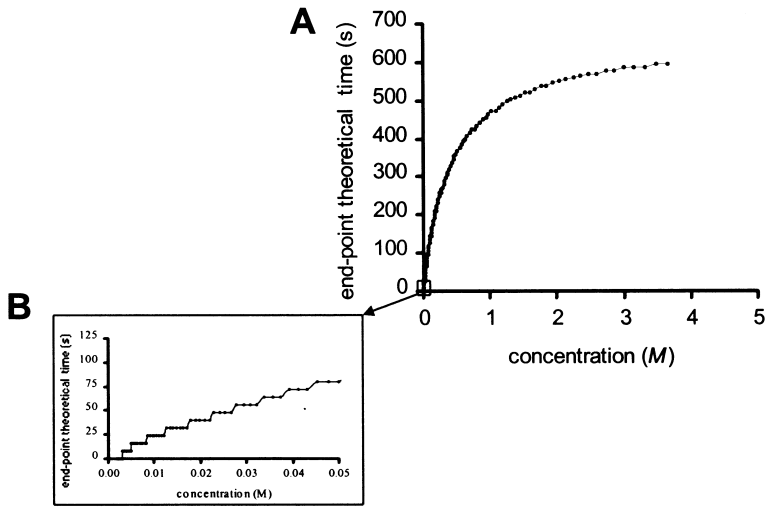

Fig. 2. (A) Theoretical end-point titration time (s) as a function of the titrand concentration (M). Each graphic point represents the previous concentration plus 5%. (B) Details of the theoretical end-point times variation for the lowest concentrations.

4. Materials and methods

4.1. Reagents and solutions

Analytical-reagent grade chemicals and deionized water with a specific conductivity of less than 0.1 μS/cm were used throughout.

Acetic and hydrochloric acid solutions used as standards were prepared from the corresponding standards by adequate dilution. The concentration of the solutions hereby obtained was determined by potentiometric titration with sodium hydroxide solution using a conventional glass electrode. This determination was performed with an automatic batch titrator.

When required, carbonate free sodium hydroxide solutions used as titrant were prepared from a concentrated solution filtered in nitrogen atmosphere [16]. Water used was heated and cooled before use, and when necessary, its ionic strength adjusted with KNO_3. Standardisation was performed by potentiometric titration with a hydrochloric acid (0.1 M) standard solution using, also, a conventional glassy electrode. This determination was also performed with an automatic batch titrator.

The samples used were commercially available in the Portuguese market.

4.2. Instrumentation and electrodes

Omnifit PTFE tubing (0.8 mm i.d.) and connectors were used for manifold conduits.

A perspex mixing chamber (of varying volume) with a magnetic stirrer was used as reactor.

A Sensorex 450C Flat Surface Combination pH/Reference Electrode (Staton; CA 90680, USA) was used as detector. The detector was placed in a low-volume flow cell.

A Valco two-position air actuated valve (Valco Instruments) controlled by a Valco digital valve interface (DIV), actuated by TTL signals, was used as switching device. This valve presented four ports, but only three were used so that the same outlet channel was operated.

A 486 microcomputer was used as control and data acquisition unit. The interface with the analytical system was made using an Advantech PCL-818L card. The control and data acquisition software was developed in Microsoft QuickBASIC 4.5.

A Crison Model 2031 microburette aspirating pump placed at the end of the line was used to aspirate the solutions.

A Crison Model 2002 digital voltmeter (±0.1 mV sensitivity) was used for potentiometric measurements. The titration curves of the prior trials were recorded by a Kipp & Zonen recorder.

4.3. Reference procedures

The determination of total acidity in vinegars was carried out by titration using sodium hydroxide as titrant and the end-point was detected optically using phenolphthalein as indicator [17].

5. Results and discussion

5.1. Flow system manifold

A schematic representation of the flow system developed is shown in Fig. 3. An automatic microburette controlled by a microcomputer and placed at the end line of the system was used to keep a constant flow. A pneumatically actuated valve, whose commutation times were controlled by a microcomputer, was used for the insertion of different titrand and titrant volumes in the system, thus establishing a direct relationship between commutation times and volumes. The different titrand and titrant volumes were inserted sequentially into the mixing chamber resulting in their immediate mixing. As detector, a flat surface combination pH/reference electrode was used. The length path between the valve and the mixing chamber and between the mixing chamber and the detector were kept at the minimum value.

5.2. Titration valve

Different commutating valves were initially evaluated in this work due to the volumes inserted in the system depending on the valve commutation times. The pneumatic valves were selected because of their robustness and working stability. The pneumatic valve was a four-way valve, but only three ways were used so that the same outlet channel was operated. The valve exhibited a reproducible and accurate behaviour

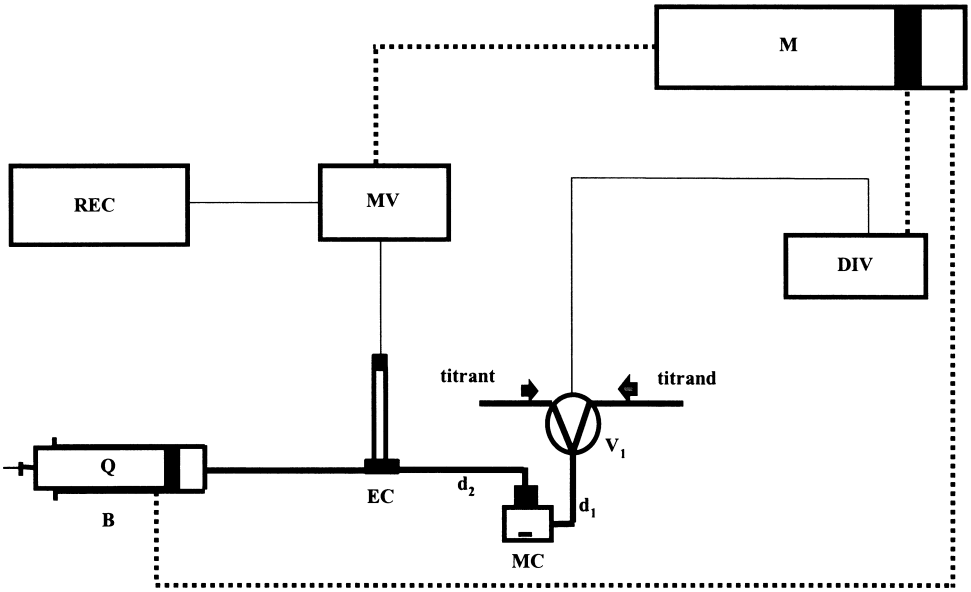

Fig. 3. Schematic representation of the manifold developed. (B) Microburette aspirating pump; EC: Flat Surface Combination pH/Reference Electrode; MV: microvoltmeter; REC: recorder; MC: mixing chamber (370 μl); *Q*: flow rate (0.46 ml/min); DIV: Valco digital valve interface; M: microcomputer; V_1: commutating valve; d_1: length path between the valve and the mixing chamber (4 cm); d_2: length path between the mixing chamber and the detector (6 cm).

for volumes higher than 2.3 μl (what was assessed by studying the commutation times and flow rates that corresponded to 0.3 s and 0.46 ml/min, respectively). The working characteristics of the valve (volumes inserted at different commutation times) were continuously evaluated throughout a long time (more than 12 months) and they were found to be stable (relative deviation (RD) < 5%) (Fig. 4).

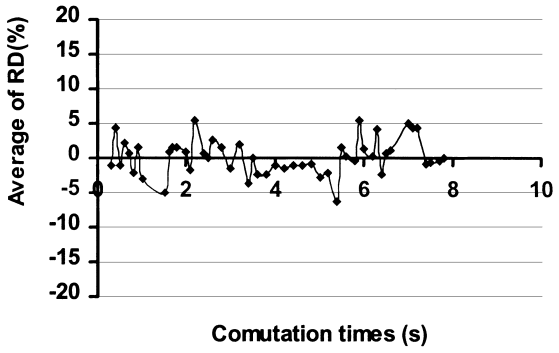

Fig. 4. Schematic representation of the average of RDs (RD%) of the volumes inserted into the system against those expected in theory regarding the several commutation times.

5.3. Automatic flow titrator

For the evaluation of the automatic flow titrator behaviour, different concentrations of acetic and hydrochloric acid standard solutions were titrated with sodium hydroxide; the titrator was afterwards applied to real samples (Fig. 5). The determination of the end-point titration time was carried out by using the second derivative (Fig. 5). The detector time (t_d) was previously evaluated and the time used in the model was 9 s.

5.3.1. Optimization

The optimization of the titration system aimed in particular at results (expressed in concentration) with relative errors of less than 5% when compared to those obtained by the reference procedure.

Based on the theoretical model previously referred to, the end-point times expected for concentrations differing by not more than 5% from each other (Fig. 2A) as well as the difference between them ($\Delta t_{5\%}$) were assessed. It was found for end-point times lower than 130 s (for titrant times between 0.3 and 7.7 s,

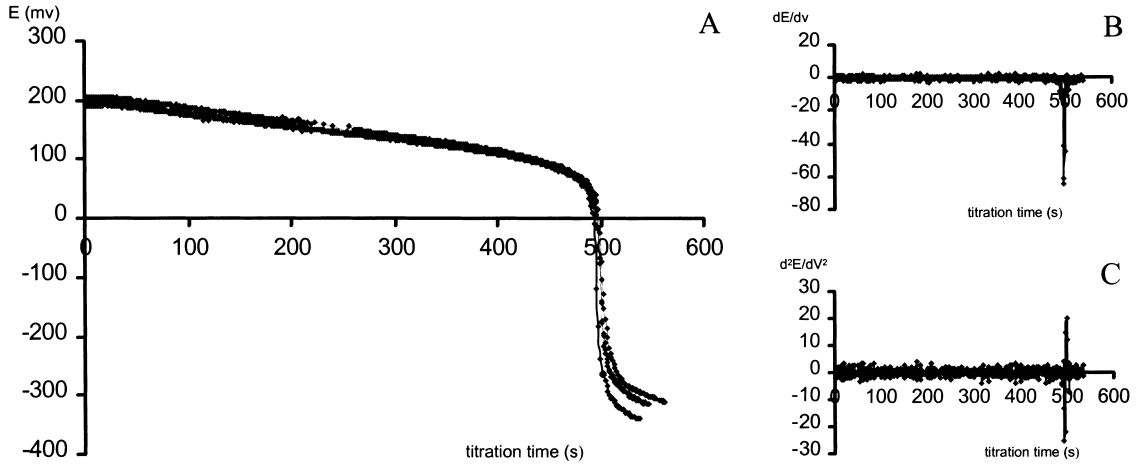

Fig. 5. Sample titration curves ($n = 4$) attained with titrant times of 0.3 s up to 7.7 s and a 0.1 s increment, a chamber volume of 370 μl and a titrant concentration of 0.5 M (A); depiction of the first derivative (B); depiction of the second derivative (C).

a 0.1 s titrant increment and 0.5 M titrant concentration) that the same end-point time was obtained for concentrations having a 5% or higher difference (Fig. 2B). Therefore, concentrations with end-point times lower than 130 s were eliminated. Calculating the $\Delta t_{5\%}$ values range ($\Delta t_{5\%\text{min}} - \Delta t_{5\%\text{max}}$) for the subsequent concentrations (also differing by 5% from each other but with different end-point times; i.e. titratable concentrations), a value of 6.5 ± 2.5 s (4–9 s range) was found (Table 1).

Titration of several standard solutions resulted in different end-point times that were then compared with those expected by the theoretical model. The differences found between theoretical and experimental times were named experimental deviations. A bias of less than 5% can be attained for these titrations if the maximum experimental deviation (maximum deviation from the theoretical model) is lower than the minimum $\Delta t_{5\%}$ value (the lowest time that separate concentrations differing by 5%).

Fig. 6A depicts the ranges of the theoretical end-point time ($T - \Delta t_{5\%\text{max}} - T + \Delta t_{5\%\text{max}}$ and $T - \Delta t_{5\%\text{min}} - T + \Delta t_{5\%\text{min}}$) corresponding to a concentration interval of ±5% for a solution of concentration M. Fig. 6B depicts the range of the experimental end-point times expected for the titration of the same solution. The determination of the whole experimental time range was carried out using the highest experimental deviation (ED_{max}), the time interval limits ($T - \text{ED}_{\text{max}}$ and $T + \text{ED}_{\text{max}}$) being calculated from the expected theoretical value (T). In order to obtain relative errors less than 5%, the experimental time range must be within the minimum theoretical time range (which means that the maximum ED value has to be equal to or less than the minimum value of the $\Delta t_{5\%}$ interval).

Table 1
Titratable concentrations range, $\Delta t_{5\%}$ and total titration time as a function of increment values (using titrant times ranging from 0.3 to 7.7 s, a total time of 8 s and a titrant concentration of 0.5 M)

Increment (s)	Titratable concentrations range (M)	$\Delta t_{5\%}$[a] (s)	Total titration time (s)
0.1	0.1–3.5	6.5 ± 2.5	600
0.2	0.2–2.0	3.5 ± 2.5	304
0.3	0.3–1.25	2.5 ± 1.9	205
0.4	0.3–0.94	1.9 ± 1.5	156
0.5	0.3–0.66	1.7 ± 1.3	126

[a] Average and standard deviation of the differences between theoretical end-point times for concentrations differing by 5%.

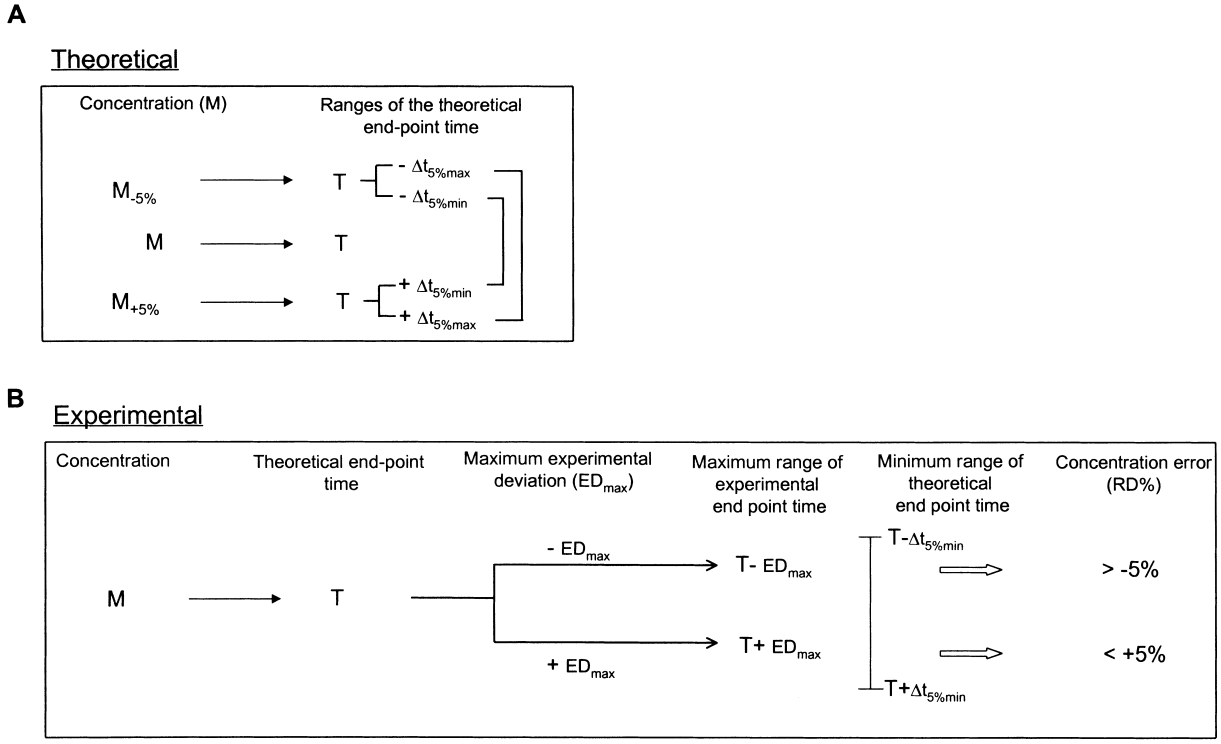

Fig. 6. (A) Theoretical end-point time ranges corresponding to a concentration interval of ±5% for a solution of concentration *M*; (B) experimental end-point time range expected for the titration of the same solution and comparison with the theoretical time interval that allow to obtain a concentration error (RD) of less than 5%.

Titrant time intervals of 0.3 of 7.7 s and a 0.1 s titrant increment (the same as the conditions used in the theoretical studies reported previously) were used for the determination of the mean experimental deviation of concentrations ranging from 0.0021 to 3.5 M, the titrant being a sodium hydroxide solution with 0.5 M concentration. In this case, the value obtained was 0.4 ± 3.9 s, $n = 32$ (Table 2). These deviations gave rise to concentration errors lower than 5% for concentrations higher than 0.1 M when a titrant concentration of 0.5 M was used (end-point titration times longer than about 130 s) because the minimum value of $\Delta t_{5\%}$ (4 s) is equal to or bigger than the maximum experimental deviation (about 4 s) (Tables 1 and 2).

The total titration time depended on the working conditions of the flow titrator which is usually related to the accuracy required of the results. This titration time decreased, keeping the same total time ($TT = T_{titrand} + T_{titrant}$) for each cycle the same initial titrant time and final titrand time, with the increment having increased (Table 1). Increasing each cycle total time, keeping the same initial titrant time, final titrand time and titrant increment results in the increase in the total titration time.

With titrant time intervals of 0.3 to 7.7 s (total time of 8 s for each cycle) and a titrant increment of 0.1 s, the total titration time was 10 min. Aiming at the reduction of the titration time, the experimental

Table 2
Experimental deviation as a function of increment values (using titrant times ranging from 0.3 to 7.7 s total time of 8 s and a titrant concentration of 0.5 M)

Increment (s)	Experimental deviations[a] (s)
0.1	0.4 ± 3.9
0.2	0.0 ± 3.2
0.3	1.9 ± 4.3
0.4	0.3 ± 3.4
0.5	1.3 ± 1.9

[a] Average and standard deviation of the difference between experimental and theoretical end-point times.

deviation was assessed as a function of titrant increment (the same initial and end times of titrant were used, i.e. 0.3 and 7.7 s and the same total time of each cycle, i.e., 8 s). However, the range of titratable concentrations and $\Delta t_{5\%}$ decreased (smaller difference between end-point times that separate the concentrations varying by 5% from each other) when the increment increased (Table 1). Therefore, performing titrations with higher increment values required a better accuracy (lower experimental deviations) of the system due to the decrease in $\Delta t_{5\%}$. Experiments showed that the accuracy was only slightly improved with the increment (Table 2). Therefore, the results could present higher than 5% errors, which determined the selection of a 0.1 s increment.

The simultaneous increase in $\Delta t_{5\%}$ and the range of titratable concentrations was obtained by increasing the total time ($TT = T_{titrant} + T_{titrand}$) of each cycle. For example, using a total time of 10 s (the initial time and the end time of titrant being 0.3 and 9.7 s, respectively), a titrant increment of 0.1 s and a titrant concentration of 0.5 M, the system operated in a concentration range of 0.077–5.5 M, with a $\Delta t_{5\%}$ of 9 ± 4 s (5–13 s range). Under these conditions, the experimental deviations obtained were -4.5 ± 7.6 s (-12–3.1 s range). These are usually higher than the $\Delta t_{5\%}$, thus producing results with a higher than 5% error regarding concentration values (ED_{max} is bigger than $\Delta t_{5\%min}$, i.e. 12 s > 5 s).

The effect of the chamber volume on the results attained has also been evaluated. The titrations of two standard solutions (0.10 and 0.19 M) carried out under the above-mentioned conditions (titrant times ranging from 0.3 to 7.7 s and a titrant increment of 0.1 s) but with different chamber volumes (350 and 430 μl) presented experimental deviations similar to those already referred to (mean experimental deviations of 4.6 and 4.7 s, for 350 and 430 μl chamber volumes, respectively).

5.3.2. Evaluation of the automatic flow titrator

Operating the titrator system under the selected conditions (titrant times ranging from 0.3 to 7.7 s, a titrant increment of 0.1 s, total time of each cycle 8 s end-point times of the solutions being higher than 130 s and a detector time of 9 s), the effectiveness of the theoretical model, repeatability, reproducibility and accuracy were evaluated.

The effectiveness of the theoretical model was proved by titrating several acetic and hydrochloric acid standard solutions (0.0050–1.6 M) with sodium hydroxide solutions (with different concentrations) for several working days ($n = 8$) and comparing the results obtained (experimental times) with those estimated by the theoretical model.

Studying the correlation of experimental times (end-point values) with the theoretical times showed that there was a good agreement (slope 1.0072, intercept -2.0804 and $R^2 = 0.9992$) for $n = 27$.

The agreement between both was also assessed by the Student *t*-test, in which the *t*-value estimated (-0.046) was lower than the tabulated one (2.05), for a confidence level of 95% ($n = 27$).

Both statistical methods showed that there were no significant statistical differences between the experimental values and those expected by the theoretical model.

Repeatability was assessed by performing replicate titrations ($n = 10$) of an acid standard solution. A relative standard deviation (RSD) of 2.6% for the concentrations was obtained.

Reproducibility was evaluated by the titration of three acid standards solution on different days ($n = 3$), which provided an RSD of 1.6–4.8%.

Accuracy was assessed by the titration of different concentrations of acetic and hydrochloric acid standard solutions. The correlation studies of the results (regarding concentration) given by the proposed and reference methods showed that there was a good agreement (the slope was 0.9902, the intercept 0.00027 and $R^2 = 0.99975$), for $n = 14$.

5.4. Determination of total acidity in vinegar samples

In order to evaluate the usefulness of this titration, the acidity determination in commercial vinegar samples was selected.

The commercial vinegar samples were titrated without prior treatment.

The results obtained with the proposed methodologies (Table 3) when compared with those given by the reference procedure showed RDs between -2.8 and 1.8%.

Repeatability was assessed by a sample consecutive titration ($n = 10$). The RSD values were 2.5%.

Table 3
Determination of total acidity in vinegar samples expressed in acetic acid (g/l)[a]

Sample	Reference method (g/l)	Proposed method (g/l)	RD (%)
1	58.23	58.72	0.8
2	59.60	58.69	−1.5
3	60.35	58.69	−2.8
4	58.24	59.55	2.2
5	57.89	58.70	1.4
6	57.65	58.69	1.8

[a] ($n = 4$); RD: relative deviation.

Reproducibility was also assessed by titrating samples (six) on different days ($n = 2$), RSD values from 3.1 to 5% being attained.

Under the working conditions selected (titrant times of 0.3–7.7 s, titrant increment 0.1 s and a total time cycle of 8 s), the total titration time was 600 s. If an end-point technique was selected, the titration time would always be lower.

The titration time was decreased (392 s) without affecting the system $\Delta t_{5\%}$ (7 ± 2.4 s) by just changing the initial and end times of the titrant (1.6 and 6.4 s, respectively, with a 0.1 s increment). The range of titratable concentrations was reduced (corresponding to a range of 0.15–1.2 M when the titrant presented a 0.5 M concentration), though the samples' concentration was still included. The results were also in good agreement with those provided by the reference method (RDs ranging from −2.1 to 4.2%).

6. Conclusions

The titration system developed allowed titrations similar to those obtained with batch titration systems. This system enabled to obtain complete titration curves, and a determination of the end point by the second derivative method like in batch titration systems. The evaluated theoretical model was appropriate for describing the analytical process and was used for the determination of the titrand concentration determination without requiring any previous calibration process.

As this system does not require any prior calibration, and presents the same advantages as the flow systems (high sampling rates, low consumption of reagents, no manual washing step of the titrator vessel and the capability of being easily automated) and allows the fully automated continuous monitoring of parameters determined by titration, it may represent an advantageous alternative to other titration procedures.

This is also a versatile system since other determinations can be easily carried out without physical reconfiguration of the manifold, except for the probable shift of the detector. Moreover, it can be coupled to other devices, for example filtration systems. Changes in the titration strategy (times used) are easily implemented by varying the titrator control parameters, enabling its adjustment to the accuracy intended. The ratio between higher and lower titratable concentrations of the proposed system may be determined by the initial and end times of the titrant and thus longer time ranges (lower initial time and higher end time of the titrant) correspond to larger titratable ranges. The $\Delta t_{5\%}$ of the system decreases with the increment increase and increases with increasing total times ($TT = T_{titrant} + T_{titrand}$) for each cycle. The total titration time decreases as the increment increases and when the titrant time range is lower.

The results obtained in the determination of total acidity in vinegar samples showed a good agreement with those given by the reference method.

Acknowledgements

The authors are grateful to the projects AMOCO (ERB-FAIR-CT96-1198) and CNPq/JNICT (910155/96-8). One of us (C.M.N.V.A.) is grateful to JNICT for the Ph.D. grant. We also thank Antonio Conceição (IST) for the discussion about dynamic models.

References

[1] J.J. Lingane, Anal. Chem. 4 (1948) 285.
[2] J.J. Lingane, Anal. Chem. 9 (1948) 797.
[3] L. Pehrsson, F. Ingman, Talanta 24 (1977) 79.
[4] W.J. Blaedel, R.H. Laessig, Anal. Chem. 8 (1964) 1617.
[5] S.M. Abicht, Anal. Chim. Acta 114 (1980) 247.
[6] B. Fleet, A.Y.W. Ho, Anal. Chem. 1 (1974) 9.
[7] J. Ruzicka, E.H. Hansan, H. Mosbaek, Anal. Chim. Acta 92 (1977) 235.
[8] A.U. Ramsing, J. Ruzicka, E.H. Hansen, Anal. Chim. Acta 129 (1981) 1.
[9] B. Fuhrmann, U. Spohn, Anal. Chim. Acta 282 (1993) 397.
[10] O. Aström, Anal. Chim. Acta 105 (1979) 67.

[11] R.H. Taylor, J. Ruzicka, G.D. Christian, Talanta 39 (1992) 285.
[12] Ll. Alerm, J. Masip, J. Garcia-Raurich, J. Bartroli, Quim. Anal. 13 (1994) 31.
[13] M.C.U. Araújo, A.V. Santos, R.S. Honorato, J. Autom. Chem. 5 (1997) 157.
[14] M. Korn, L.F.B.P. Gouveia, E. de Oliveira, B.F. Reis, Anal. Chim. Acta 312 (1995) 177.
[15] P.B. Martelli, B.F. Reis, M. Korn, J.L.F. Costa Lima, Anal. Chim. Acta 387 (1999) 165.
[16] I.M. Kolthoff, V.A. Stenger, Volumetric Analysis II, 2nd Revised Edition, Interscience, New York, 1947, p. 69.
[17] Official Methods of Analysis of the Association of Official Analytical Chemists, 15th Edition, Association of Official Analytical Chemists, Arlington, VA, USA, 1990, p. 1008.
[18] M. Valcarcel, M.D. Luque de Castro, Flow-Injection Analysis. Principles and Applications, Ellis Horwood, Chischester, 1987, p. 244.