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Precipitation titrations using an automatic titrator based on a multicommutated unsegmented flow system

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An automatic flow titrator based on a multicommutated unsegmented flow system was used to perform precipitation titrations with potentiometric detection. The titration approach is based on sequential introduction of increasing titrant and decreasing titrand volumes into a mixing chamber. The system allows the attainment of complete curves, the titration end point being determined by the Gran method, as is usually employed in batch potentiometric titrations. The theoretical model for the analytical process is presented and discussed and the determination of titrand concentration is performed without any prior calibration. The automatic flow titrator developed was applied to chloride determination in bottled natural waters and the results obtained were reproducible (RSD 3.2 and 3.8% for repeatability and reproducibility, respectively) and in good agreement with those given by the reference procedure (relative deviation within the range from −4.6 to 4.8%).

Introduction

Titrimetric analysis techniques are widely used in laboratories and in the control of various industrial processes. The time-consuming and labour-intensive operations stemming from the batchwise mode of performing titrations, as well as the troublesome processes of collecting and plotting the data sometimes required for the titration curve, are some of the main drawbacks of titrimetric procedures. The above reasons could justify the use of titrations only when direct measurement does not yield acceptable results and why researchers are interested in the automation of the titration procedure.

First, batch titration systems were partially[1,2] or totally[3] automated. However, as these systems required elaborate and expensive equipment, several workers then proposed continuous flow systems. Blaedel and Laessig[4] described a continuous titrator in which the sample is pumped at a constant flow rate and the reagent stream at a variable flow rate. After mixing, the resultant stream passes through the detector. By adjusting the speed of the reagent pump, the mixed stream can be made to attain the equivalence point composition.

A gradient titration technique was developed by Fleet and Ho,[5] involving the semi-continuous monitoring of a sample stream with a reagent stream in which the concentration of the reagent increases linearly in the form of a gradient. Nagy *et al.*[6] developed the 'triangle-programmed titration' technique. In this methodology, the titrant concentration is first linearly increased and then decreased in a symmetrical way, thus obtaining two equivalence points.

Continuous single-point titrations have been proposed by Astrom,[7] involving the use of a peristaltic pump; two channels were used so that equal buffer and sample flows were mixed. Measurements were made on the effluent after mixing in a conventional titration vessel. Ruzicka and co-workers[8,9] developed the flow injection titration (FIA titration) method, in which the time between the stoichiometric points for the rising and falling parts of the titration curve is proportional to the logarithm of the concentration.

Valcárcel *et al.*[10,11] have used flow rate gradients to generate concentration gradients. They combined a fixed flow rate pump with a programmed flow rate pump that was used to increase gradually the titrant concentration in the flow system.

A flow injection analysis technique based on stop flow coulometric titration was developed by Taylor *et al.*[12] This technique uses a gradient chamber, a reagent generation chamber, and a detector flow cell integrated into a single unit. By stopping the flow at a suitable delay time, following sample injection, the sample zone will be held inside the mixing chamber, allowing automatic dilution prior to titration. If the detection and the coulometric reagent generation are performed inside the mixing chamber, all sample material will react, as in conventional titrimetry.

Araújo *et al.*[13] presented a flow injection titration based on a concentration gradient with a single standard calibration. In this flow manifold, the concentration of one of the solutions (sample or titrant) is kept at its steady state during the whole process, by pumping it continuously. The other solution is injected and its concentration determined by the gradient calibration technique.

All the above-mentioned flow titration techniques require a calibration process for the attainment of the unknown concentration.

A binary search strategy for the end point determination using a multicommutated flow system was proposed by Korn *et al.*[14] and promoted the development of unsegmented[14] or segmented[15,16] flow titrations. This method is based on variable volumetric ratios between the titrant and sample solution selected by a binary algorithm. Although these titrations do not require any calibration, they were only applied to systems in which an indicator[14,16] or other reference solutions[15] can be used by the binary searching algorithm to decide the next step in the searching process.

In this work, a flow titration strategy based on the unsegmented sequential introduction into a reactor (mixing chamber) of increasing volumes of titrant and decreasing volumes of titrand is used to perform titrations without

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requiring a calibration step. This flow system enables one to attain complete titration curves similar to those of batch titration systems, allowing more data to be obtained during the titration process which could be used for several purposes, *e.g.*, equilibrium studies. The software to control every step of the titration procedure, perform data acquisition and data processing was also developed.

The equivalence point in a batch potentiometric titration is generally determined by finding the point of maximum slope of the titration curve. In many instances there are very sharp breaks in these curves and, therefore, no difficulty in finding the equivalence point. However, in other cases, the curves are hardly evaluated because the potential variation is small close to the equivalence point. It is then usual to use the Gran method[17,18] which renders the titration curves linear, thereby making possible the determination of the equivalence volume by using several points on the titration curve, instead of only the inflection point. The applicability of this end point location method is also evaluated in this work by using the automatic flow titrator presented.

The model[19] used for the determination of the theoretical end point time for each titrand standard concentration was tested and proved to be suitable for the description of the analytical process.

The flow system proposed allows one to simulate batch titration procedures without requiring a calibration step because the determination of the unknown titrand concentration is carried out by an iterative procedure, which, based on the equations of the theoretical model,[19] estimates the titrand concentration whose theoretical end point time corresponds to the experimental value.

In order to evaluate the usefulness of the developed titration system, chloride determination in bottled natural waters was selected as it is a parameter determined in the quality control of waters and where direct potentiometry cannot usually be used. The results given by the proposed and reference methods showed a good agreement.

Experimental

Reagents and solutions

All chemicals used were of analytical-reagent grade and deionised water with a specific conductivity less than 0.1 μS cm^{-1} was used throughout.

Chloride standard solution was prepared from its salts previously dried and the most diluted solutions were obtained by dilution of the former.

Silver nitrate solutions used as titrant were standardized by potentiometric titration with a chloride standard solution. This determination was performed with an automatic batch titrator.

The potentiometric determinations were carried out using potassium nitrate (0.1 M) for the ionic strength adjustment of standard solutions (chloride standard solution and silver nitrate), when necessary, and nitric acid (10^{-3} M) to prevent the silver hydroxide and oxide precipitation of the silver nitrate.

The bottled samples used were commercially available on the Portuguese market and had no prior treatment.

Instrumentation and apparatus

Omnifit Teflon tubing (0.8 mm id) and connectors were used for manifold conduits.

A Perspex mixing chamber with a magnetic stirrer was used as reactor.

A double-junction Orion 90-0029 reference electrode with a 0.1 M KNO_3 solution in the outer compartment and a tubular-shaped silver(I) ion-selective electrode with a homogeneous crystalline membrane[20] as indicator electrode were used. The sensor membrane of the tubular electrode was renewed from time to time by polishing with a damp cotton cloth and aluminium powder (BDH, 3 μm).

Owing to the volumes introduced into the system depending on the valve commutation times, different commutating valves were initially evaluated. A Valco two-position air actuated valve (Valco Instruments) controlled by a Valco digital valve interface (DIV), actuated by TTL signals, was selected as the switching device. This valve presented four ports but only three were used so that the same outlet channel was operated. The minimum volume introduced into the system in an accurate and reproducible manner was 2.3 μL (which was assessed by studying the commutation times and flow rates that corresponded to 0.3 s and 0.46 mL min^{-1}, respectively). The working characteristics of the valve (volumes introduced at different commutation times) were evaluated for over 12 months and they were found to be stable (relative deviation ≤5%).

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

A Crison Model 2031 microburette was used as the pump and placed at the end of the line.

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.

Reference procedure

The reference method[21] used for the determination of chloride in waters consists in potentiometric titration with silver nitrate using a glass and silver–silver chloride electrode system. This work resorted alternatively to a conventionally shaped silver electrode[20] and an Orion Model 90-0029 double-junction AgCl–Ag reference electrode. This titration was performed by using an automatic batch titrator.

Results and discussion

Theoretical aspects

1. Titration strategy. The strategy proposed is based on the sequential introduction of increasing titrant and decreasing titrand volumes into a reactor (a mixing chamber), the introduced 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 volume change can be determined from the time values.

A schematic representation of the titration strategy is shown in Fig. 1. 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. 1B).

Prior to titration, some parameters are set, such as initial (t_i) and final (t_f) titrant time, total time of each cycle (t_T, *i.e.* $t_s + t_t$, kept constant throughout titration) and the titrant increment (*Inc*). The titrand times along the titration correspond to the remainder left after subtracting the titrant time from the total time of each cycle.

First, the reactor is filled with titrand (Fig. 1A and B, step 1). Once titration has been started the first titrant volume (which corresponds to a certain commutation time, named t_i) is introduced into the reactor (Fig. 1A and B, step 2). The former titrant time (t_i) is the same as or higher than the lowest time, allowing the introduction of an accurate volume (minimum

volume) through the valve. The titrant introduction causes a titrand concentration reduction at the mixing chamber.

The next step (Fig. 1A and B, step 3) corresponds to the introduction of a titrand volume (which corresponds to a certain commutation time, named t_s). The titrand volumes (or titrand times) correspond to the remainder left after subtracting the titrant volume (or titrant time) from the total volume (or total time) of each cycle ($t_s = t_T - t_t$). The introduction of titrand promotes an increase of the titrand concentration in the reactor that is usually smaller than the expected reduction derived from the introduction of titrant. The first cycle is thereby ended.

This procedure is performed repeatedly (n cycles) until the titrant time reaches the final time (t_f), the titrant volumes introduced into the reactor being progressively higher (by a fixed increment) and the titrand volumes progressively lower (Fig. 1A).

The data attained from the titration process are stored in a local file for data processing, namely end point calculation. The detector reaching time (which corresponds to the time necessary for the sample to reach the detector) is subtracted from the titration end point time obtained.

2. Titration model. As already mentioned, it was assumed that the reactor (mixing chamber) is initially full of titrand. The variation (reduction) of its concentration during introduction of titrant (Fig. 1B, step 2) can be expressed[19] by:

$$Cs(t_x) = \left(-\frac{C^0\mathrm{t}}{n}\right) + \left(\frac{C^0\mathrm{t}}{n} + Cs(t_{y1})\right)\exp\left(-\frac{F}{V}(\Delta t_\mathrm{t})\right) \quad (1)$$

where $Cs(t_x)$ is the variation of titrand concentration (mol L^{-1}) in the mixing chamber while titrant is being introduced; C^0t the initial titrant concentration (mol L^{-1}); $Cs(t_{y1})$ the titrand concentration (mol L^{-1}) in the mixing chamber before the introduction of titrant (for $t = 0$ it is the same as the initial titrand concentration); F the flow rate (L s^{-1}); V the chamber volume (L); (Δt_t) the time (s) for titrant introduction into the mixing chamber; and n the stoichiometric coefficient of the reaction (titrand/titrant).

The variation (increase) of titrand concentration over the introduction of titrand into the mixing chamber (Fig. 1B, step 3) can be expressed[19] by:

$$Cs(t_y) = C^0\mathrm{s} - \left(C^0\mathrm{s} - Cs(t_{x1})\right)\exp\left[-\frac{F}{V}(\Delta t_\mathrm{s})\right] \quad (2)$$

where $Cs(t_y)$ is the variation of titrand concentration (mol L^{-1}) in the mixing chamber throughout titrand introduction; C^0s the initial titrand concentration (mol L^{-1}); $Cs(t_{x1})$ the titrand concentration in the mixing chamber after introduction of titrant

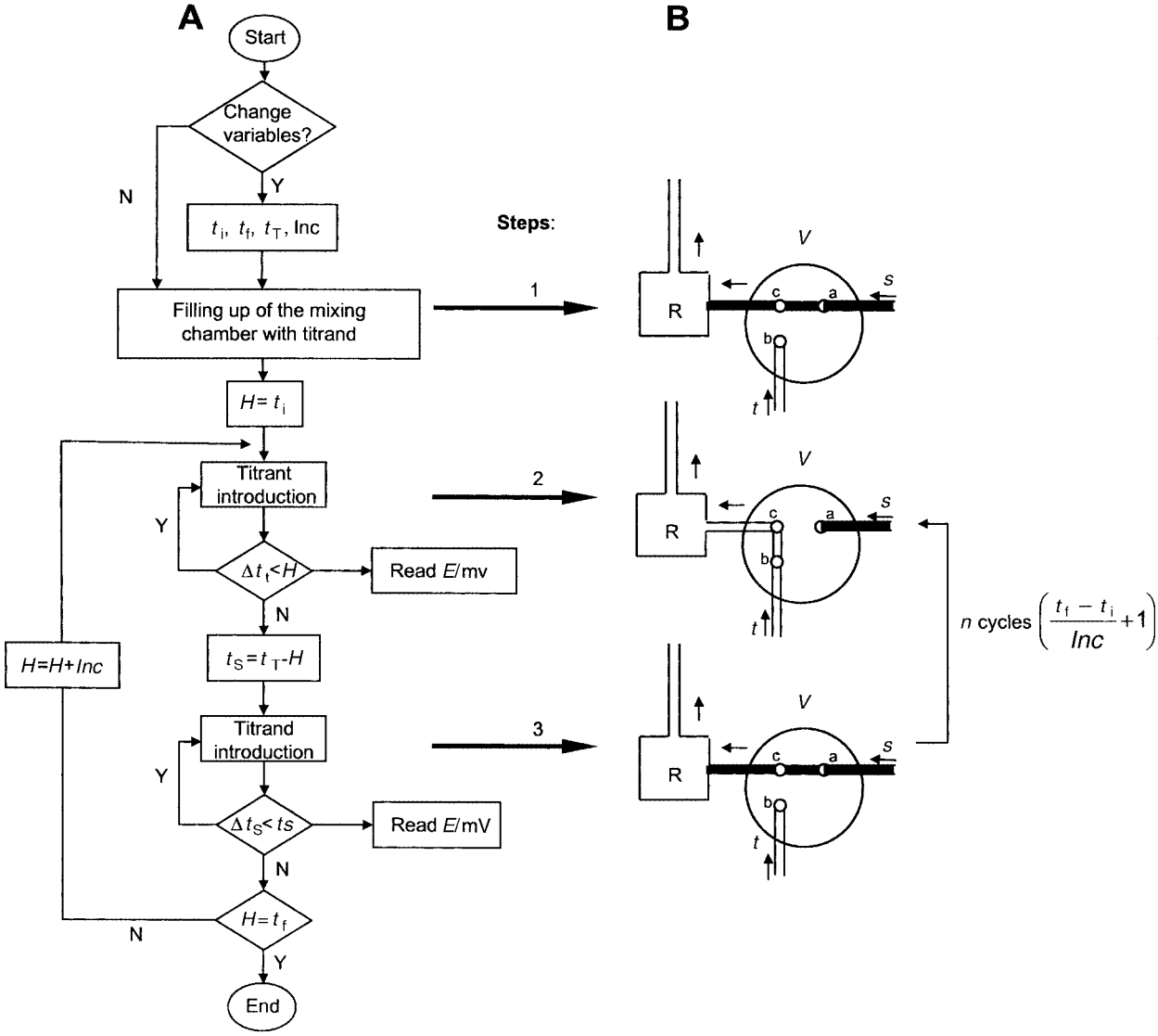

Fig. 1 Schematic representation of the titration strategy. (A) Algorithm flow chart of the titration. t_i and t_f: Initial and final titrant times, respectively; t_s: titrand time (corresponds to the remainder left after subtracting the titrant time from the total time of each cycle); t_T: total time of each cycle; *Inc*: titrant increment. (B) Illustration of the titration strategy, 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); n cycles (the number of times a given titrant and titrand volume is introduced into the system).

(just before the introduction of titrand); F the flow rate (L s^{-1}); V the chamber volume (L); and (Δt_s) the time of titrand introduction into the mixing chamber.

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

The determination of the theoretical end point time for each titrand standard concentration is based on eqn. (1) (during introduction of titrant) and (2) (during introduction of titrand), and corresponds to the titration time spent until the titrand excess switches to titrant excess. The theoretical end point time will correspond to the titration time when a constant excess of titrant is attained because there is the possibility of a brief occurrence of an excess of titrant that is consumed by the next introduction of titrand.

3. Linearization of titration curves. The determination of the experimental end point time was made with the support of a method usually employed for assessing the equivalence volume in batch potentiometric titrations, this being the Gran method. When this method is applied to titrimetric data two functions are derived: one for the readings obtained before the equivalence point and the other for the readings after the equivalence point. Each function is linearly dependent on the volume of titrant and both equal zero at the equivalence point. Thus, the volume required to reach this point can be located from the intercept of one or both lines with the volume axis.[17,18]

In the automatic flow titrator, the concentration (titrand or titrant) in the mixing chamber is estimated by means of the equations described previously [eqn. (1) (2)] and next pointed out as $Cs(t_x$ or $t_y)$.

Therefore, for the precipitation titration of Cl^- with Ag^+ we have before the end point time:

$$t_E - t = Cs(t_x \text{ or } t_y) = [Cl^-] = K_{ps}/[Ag^+] \quad (3)$$

and after the end point time:

$$t - t_E = -Cs(t_x \text{ or } t_y) = [Ag^+] \quad (4)$$

At the end point time:

$$Cs(t_x) = 0 \quad (5)$$

If $[Ag^+]$ is measured potentiometrically, *e.g.*, with a tubular-shaped silver(I) ion-selective electrode, the modified Nernst equation is:

$$E = const + S \log [Ag^+] \quad (6)$$

Then, (eqn. 3) and (4) can be expressed as follows:

$$t_E - t = K_1 \times 10^{-E/S} \quad (3a)$$

$$t - t_E = K_2 \times 10^{E/S} \quad (4a)$$

where E is the measured value of E_{cell} and S is the calibration slope of the electrode.

It is not necessary to know the absolute values of *const* (the standard electrode potential, reference electrode potential and junction potential) or K_{ps} because these parameters can be included in the K_1 and K_2 constants which may be arbitrarily chosen. The value of S should be previously estimated.

When eqn. (3a) and (4a) are plotted as functions of titration time, two straight lines are obtained. These lines intersect each other theoretically on the t-axis at the end point time (t_E).

4. Determination of titrand concentration. The determination of the unknown titrand concentration is carried out by an iterative procedure that, based on the equations [eqn. (1) and (2) of the theoretical model, estimates the titrand concentration whose theoretical end point time corresponds to the experimental value. Therefore, the necessary subroutine allowing the determination of titrand concentration was implemented. The algorithm developed is shown in a flow chart (Fig. 2). This subroutine determines the theoretical end point titration time corresponding to a simulated concentration interval. For the calculation, parameters such as initial titrant concentration (C^0t), mixing chamber volume (V), flow rate (F), initial (T_i) and final (T_f) titrant time, total time of each cycle (T_T), titrant increment (*Inc*) and stoichiometric coefficient of the reaction (n) must be known. Parameters such as simulated theoretical initial concentration (C) and concentration increment (C_{Inc}) must be chosen.

After each assessment, the theoretical end point time obtained (T) and the experimental end point time (T_E) are compared. If the value of T found is lower than the experimental value ($T < T_E$), the system moves on to the next concentration ($Cs = Cs + C_{inc}$) for the assessment of the new theoretical end point titration time. Only when the time assessed matches the experimental value ($T = T_E$) does the titrand concentration correspond to the theoretical value ($C_{titrand} = Cs$).

5. Accuracy model. The optimisation of the automatic flow titrator system is mainly dependent on the accuracy required for the results. The determination of a certain solution concentration with a maximum error (relative deviation) of ±X%, requires the attainment of the theoretical time range of that error (Fig. 3A) as well as to know if the experimental values are within that range (Fig. 3B).

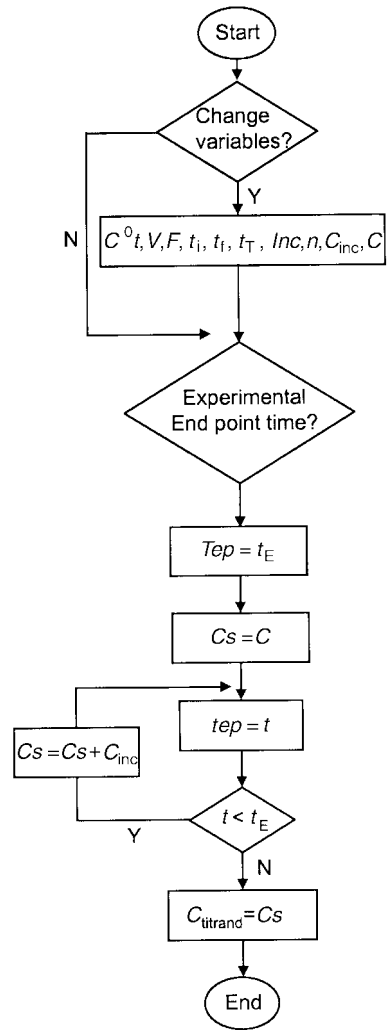

Fig. 2 Algorithm flow chart for the determination of titrand concentration. C^0t: Initial titrant concentration; V, chamber volume; F, flow rate; T_i and T_f: initial and final titrant times,respectively; T_T: total time of each cycle; n: stoichiometric coefficient of the reaction; C_{inc}: concentration increment value; and C: theoretical initial concentration.

To find the theoretical time range of the error (±*X*%) it is initially necessary to calculate, based on the theoretical model described earlier, the end point times expected for concentrations differing by *X*% from each other, as well as the difference between them ($\Delta t_{X\%} \pm \sigma\Delta t_{X\%}$, which corresponds to the average and the standard deviation of the time differences). Only concentrations differing by *X*% from each other and with different end point times, *i.e.* titratable concentrations, are considered in this calculation (concentrations differing by *X*% with the same end point time are excluded). The theoretical end point time ranges corresponding to a concentration interval of ±*X*% for a solution of concentration *M* (error ranges) can be calculated based on the $\Delta t_{X\%} \pm \sigma\Delta t_{X\%}$ value ($t - \Delta t_{X\%max}$–$t + \Delta t_{X\%max}$ and $t - \Delta t_{X\%min}$–$t + \Delta t_{X\%min}$ ranges, *t* being the theoretical end point time for the concentration *M*) (Fig. 3A).

The experimental end point times obtained when the same solution (concentration *M*) is titrated must be within the minimum theoretical end point time range, *i.e.* $t - \Delta t_{X\%min}$–$t + \Delta t_{X\%min}$ that establishes the minimum length, expressed as time, between concentrations differing by *X*% from each other, so as to assure errors less than *X*% (Fig. 3B). The evaluation of the accuracy of the experimental values is made by titration of several standard solutions and subsequent comparison of the different end point times obtained with those expected by the theoretical model. We call the differences found between theoretical and experimental times, experimental deviations (*ED*, meaning the expected deviations relative to the theoretical *t* value). The determination of the whole experimental time range expected for any concentration (in this example with the *M* value) is carried out by using the highest experimental deviation (ED_{max}) of the experimental deviation range ($ED \pm \sigma_{ED}$) obtained with the standard solutions, the time interval limits ($t - ED_{max}$ and $t + ED_{max}$) being calculated from the expected theoretical end point value (*t*) (Fig. 3B). In order to obtain relative errors less than *X*%, the whole experimental time range expected for any concentration must be within the minimum theoretical time range of the error (meaning that the ED_{max} value has to be equal to or less than the $\Delta t_{X\%min}$ value) (Fig. 3B).

Automatic flow titrator manifold

A schematic representation of the flow system developed is shown in Fig. 4. The flow rate was kept constant by using an automatic burette placed at the end line of the flow system. A pneumatically actuated valve was used for the introduction of different titrand and titrant volumes, the commutation times being controlled by a microcomputer (there being a direct relationship between commutation times and volumes). The different titrand and titrant volumes were sequentially introduced into the mixing chamber resulting in their immediate mixing. The monitoring of the analytical signal was accomplished by a tubular-shaped ion-selective electrode. The length of the connection path from the valve to the mixing chamber and from the latter to the detector was kept at the minimum value.

System optimisation

For the evaluation of the automatic flow titrator behaviour, different concentrations of chloride standard solutions were titrated with silver nitrate solution, the titrator being subsequently applied to real samples. The determination of the end point titration time was carried out by the Gran method. The detector reaching time previously evaluated and used was 10 s.

By application of the Gran method to the experimental data [(Fig 5(a)], the curve shown in Fig. 5(b) is obtained.

Two different end point times were obtained with the two straight lines resulting from the linearization method. The experimental end point times were assessed by means of eqn. (4a) as the results thereby provided are much closer to those theoretically expected and the best working conditions of the electrode are found here because, before reaching the titration end point, silver concentrations inside the mixing chamber are lower than the inferior limit of linear response of the electrode[20] (in spite of being linearized the electrode slope at this zone is possibly lower than that of the remainder of the titration). The slope of the tubular-shaped silver(I) ion-selective electrode was previously determined.

The optimization of the titration system was aimed particularly at the attainment of results with relative deviation less than 5% when compared with those obtained by the reference procedure.

Based on the theoretical model described earlier, the theoretical end point times expected for concentrations differing by 5% from each other were assessed as well as the difference between them ($\Delta t_{5\%} \pm \sigma\Delta t_{5\%}$). For end point times lower than 130 s, using titrant time intervals between 0.3 s (t_i) and 7.7 s (t_f),

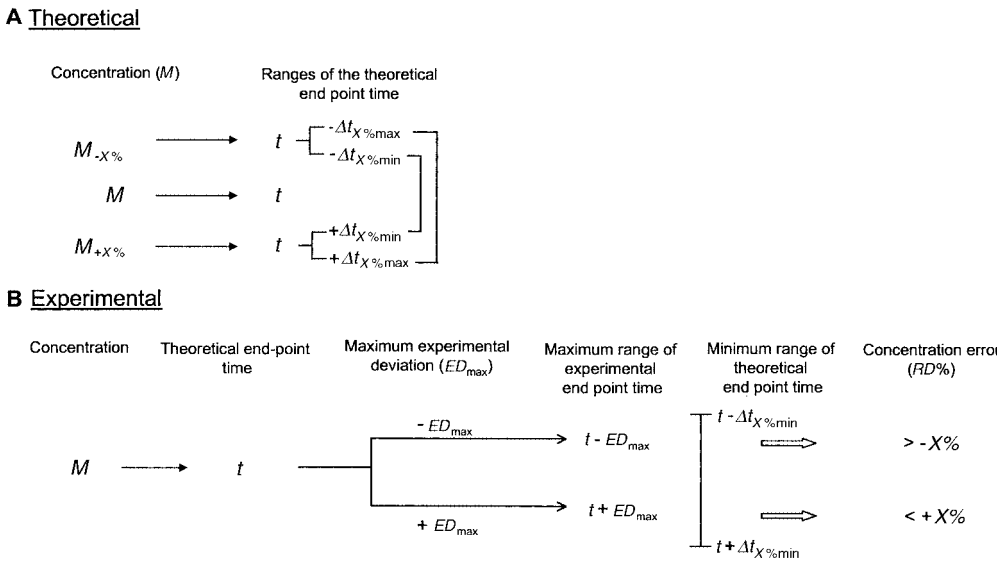

Fig. 3 (A) Theoretical end point time ranges corresponding to a concentration interval of ±*X*% for a solution of concentration M. (B) Experimental end point time range expected for the titration of the same solution and comparison with the theoretical time interval that allows one to obtain a concentration error (*RD*) less than X%.

with a total time of each cycle (t_T) of 8 s and a titrant time increment (*Inc*) of 0.1 s, the same end point time was obtained even for concentrations differing by more than 5% from each other. Therefore, concentrations with end point times lower than 130 s were not used in this calculation. By calculating the $\Delta t_{5\%}$ values range ($\Delta t_{5\%min}$–$\Delta t_{5\%max}$) 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 (experimental deviation). An accuracy of less than 5% (relative deviation) 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 distinguishes concentrations differing by 5% from each other). Titrant time intervals between 0.3 s (t_i) and 7.7 s (t_f), with a total time of each cycle (t_T) of 8 s and a titrant time increment (*Inc*) of 0.1 s (the same conditions used in the theoretical studies reported previously), were used for the determination of the experimental deviation of concentrations ranging from 2 to 110 mg L^{-1} (titratable concentrations), the titrant being a silver nitrate solution with 3.49×10^{-4} or 1.05×10^{-3} M concentration. In this case the value obtained was 0.8 s ± 2.8 s, n = 37 (Table 2). These deviations gave rise to concentration errors lower than 5% (relative deviation), since deviations of 6.5 ± 2.5 s can be accepted within this concentration range, which means that the minimum value of $\Delta t_{5\%}$ (4 s) is equal to or higher than the maximum experimental deviation (3.6 s).

The total titration time depended on the initial (t_i) and final (t_f) titrant times, total time of each cycle (t_T) and titrant increment (*Inc*) used. Using titrant times of 0.3 s (t_i) to 7.7 s (t_f), a total time for each cycle (t_T) of 8s and a titrant time increment (*Inc*) of 0.1 s, the total titration time was 600 s. Aiming at the reduction of the titration time but with the same accuracy of results (relative deviation less than 5%), the experimental deviation was assessed as a function of titrant time increment (the same initial and final titrant times were used, *i.e.* 0.3 and 7.7 s and an increment of 0.2 and 0.3 s) (Table 2). Nevertheless, theoretically, the range of titratable concentrations and $\Delta t_{5\%}$ decreased (smaller concentration range and smaller difference between end point times that distinguish concentrations varying by 5% from each other, respectively) 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 of $\Delta t_{5\%}$ (smaller $\Delta t_{5\%min}$ values). Experiments showed that accuracy decreases (larger ED_{max} values) with the increase of the titrant time increment (Table 2). Therefore, the results presented errors higher than 5%.

The titratable concentration ranges and $\Delta t_{\%}$ values increase if a lower accuracy is accepted for the results (10 and 15% for the relative deviation values, for example). The increase of the former occurs due to the different end point times with

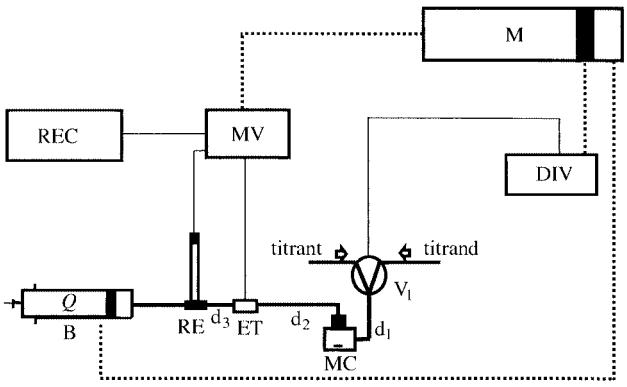

Fig. 4 Schematic representation of the manifold developed. B: Burette aspirating pump; ET: tubular-shaped silver(I) ion-selective electrode; RE: double-junction Orion 90-0029 reference electrode; MV: voltmeter; REC: recorder; MC: mixing chamber (370 μL); Q: flow rate (0.46 ml min^{-1}); DIV: Valco digital valve interface; M: microcomputer; V_1: commutating valve; d_1: length of path between the valve and the mixing chamber (4 cm); d_2: length of path from the mixing chamber to the ion-selective electrode (6 cm); d_3: length of path from the ion-selective electrode to the reference electrode (3 cm).

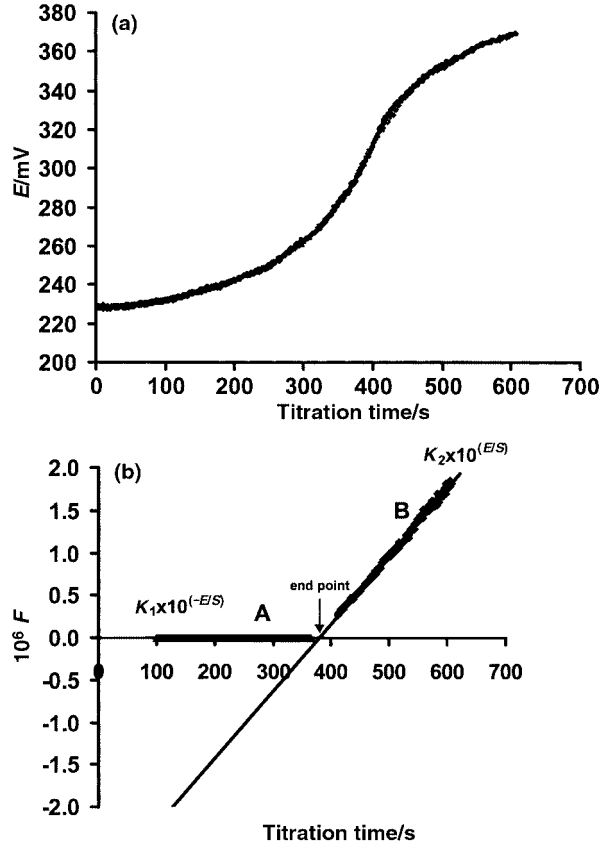

Fig. 5 (a) Sample titration curves (n = 4); (b) linear transformed titration curves obtained when data from (a) are evaluated by use of eqn. (3a) for branch A ($y = 1.51 \times 10^{-10} x + 5.89 \times 10^{-8}$, R^2 = 0.9965) and eqn. (4a) for branch B ($y = 7.98 \times 10^3 x - 3.02 \times 10^6$, R^2 = 0.9974).

Table 1 Theoretical titratable concentration ranges and $\Delta t_{X\%}$ (5, 10 and 15%) as a function of titrant time increment values (0.1, 0.2 and 0.3 s) for concentrations differing by 5, 10 and 15% (0.3, 7.7 and 8 s being the t_i, t_f and t_T values used, respectively, and 3.49×10^{-4} M the titrant concentration)

	Concentrations differing by 5%		Concentrations differing by 10%		Concentrations differing by 15%	
Increment/s	Titratable concentrations range/mg L^{-1}	$\Delta t_{5\%}$/s[a]	Titratable concentrations range/mg L^{-1}	$\Delta t_{10\%}$t/s[a]	Titratable concentrations range/mg L^{-1}	$\Delta t_{15\%}$t/s[a]
0.1	2.0–90.0	6.5±2.5	0.82–90	10.8±4.3	0.5–90	15.4 ± 5.8
0.2	5.0–53.0	3.5±2.5	1.33–50	6.4±2.5	1.0–50	9.0 ± 3.4
0.3	7.1–32.3	2.5±1.9	3.4–31	4.9±2.4	1.5–33	6.8 ± 2.2

[a] Average and standard deviation of the differences between theoretical end point times for concentrations differing by 5, 10 and 15%.

concentrations differing by 10 or 15%, which firstly occurs in lower concentrations; the $\Delta t_{\%}$ increases because the difference (in terms of time) between concentrations differing by 10 or 15% is larger (Table 1). The experimental deviations obtained from higher increments (maximum deviations of 8.8 and 9.6 s given by 0.2 and 0.3 s increments, respectively) confirm that the results might reach over 15% errors (Tables 1 and 2).

The simultaneous increase of $\Delta t_{5\%}$ and the titratable concentrations range (concentrations differing by 5%) can also be obtained by increasing the total time of each cycle ($t_T = t_s + t_t$) (without changing the initial titrant time, the final titrand time and the titrant time increment). For example, using a total time of 10 s (the initial and final titrant times being 0.3 and 9.7 s, respectively), a titrant time increment of 0.1 s and a titrant concentration of 3.5×10^{-4} M, the system operates theoretically within a concentration range from 1.7 to 135.3 mg L^{-1}, with a $\Delta t_{5\%}$ of 9 ± 4 s (5–13 s range). Under these conditions, the experimental deviations obtained were -8.6 ± 11 s (-19.6–2.4 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 larger than $\Delta t_{5\%min}$, *i.e.* 19.6 > 5 s).

The effect of the chamber volume on the results attained was also evaluated. The titrations of three standard solutions (3.41, 6.37 and 16.1 mg L^{-1}) carried out under the above-mentioned conditions (titrant times ranging from 0.3 to 7.7 s, a total time of each cycle of 8 s and an increment of 0.1 s) but with different chamber volumes (273 and 370 μL) presented experimental deviations similar to those described above (ED_{max} of 3.5 and 4.2 s, for 273 and 370 μL chamber volumes, respectively). Theoretically, the accuracy of the system is only affected when the chamber volume differs by more than 40 μL from the value used in the model, which represents a reasonable independency between the accuracy of the system and the exact knowledge of the chamber volume.

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 total time of each cycle of 8 s, a titrant time increment of 0.1 s, end point times of the solutions being higher than 130 s and a detector time of 10 s), the effectiveness of the theoretical model, and also repeatability, reproducibility and accuracy was evaluated.

The effectiveness of the theoretical model was proved by titrating several chloride standard solutions (2–110 mg L^{-1}) with silver nitrate solutions (3.49×10^{-4} and 1.05×10^{-3} M) for several working days ($n = 9$) and comparing the experimental and theoretical end point times.

Studying the correlation of experimental times with the theoretical times showed that there was a good agreement between both (slope 1.0078, intercept −1.6366 and R^2 = 0.9994) for $n = 37$.

This agreement between both values was also assessed by the Student's paired *t*-test, in which the *t*-value estimated (1.68) was lower than the tabulated value (2.03), for a confidence level of 95% ($n = 37$).

Table 2 Experimental deviations (*ED*), maximum experimental deviation (ED_{max}) and total titration time as a function of titrant time increment values (0.3, 7.7 and 8 s the t_i, t_f and t_T values used, respectively, and 3.49×10^{-4} M or 1.05×10^{-3} M the titrant concentration)

Increment/s	Experimental deviations/s[a]	ED_{max}	Total titration time/s
0.1	0.8 ± 2.8	3.6	600
0.2	6.0 ± 2.8	8.8	304
0.3	4.1 ± 5.5	9.6	205

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

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

Repeatability was assessed by performing replicate titrations ($n = 11$) of a chloride standard solution. A relative standard deviation (RSD) of 1.7% for the concentrations was obtained.

Reproducibility was tested by titration of a chloride standard solution on different days ($n = 8$) for 4 weeks, and provided an RSD of 2.4% for the concentrations.

Accuracy was evaluated by comparing the concentration results (range of concentrations titratable by the system) given by the proposed and reference methods using several chloride standard solutions. The correlation studies showed that there was a good agreement (slope 1.0018, intercept 0.2879 and R^2 = 0.9976), for $n = 37$.

Chloride determination in bottled natural waters

The automatic flow titrator was used, under the selected conditions, for chloride determination in bottled natural waters without prior treatment, using a silver nitrate solution with a 3.49×10^{-4} M concentration (Fig. 5).

The results obtained with the proposed method (Table 3) when compared with those given by the reference method showed relative deviations between −4.6 and 4.8%. The correlation studies of the results given by the proposed and reference methods showed that there was a good agreement (slope 1.0542, intercept −0.3085 and R^2 = 0.9977), for $n = 10$. The agreement between both values was also assessed by the Student's paired *t*-test, in which the *t*-value estimated (−0.84) was lower than the tabulated value (2.26), for a confidence level of 95% ($n = 10$).

Repeatability was assessed by consecutive titration ($n = 10$) of a sample. The RSD was 3.2%.

Reproducibility was also assessed by titrating the same sample on different days ($n = 4$), an RSD of 3.8% being attained.

Conclusions

The automatic flow titrator developed based on a multicommutated unsegmented flow system presents working characteristics similar to those of batch titration systems and unlike other flow systems does not require any prior calibration. The applicability of the Gran method was shown to be an adequate process for end point determination.

The system enables one to obtain complete titration curves allowing a large number of data points to be achieved which could be used for several purposes, *e.g.*, equilibrium studies.

Table 3 Results obtained in the determination of chloride in bottled natural waters, by the proposed method and by the reference method.

Sample	Reference method/ mg L^{-1}[a]	Proposed method/ mg L^{-1}[a]	*RD*(%)[b]
1	8.91 ± 0.43	9.16 ± 0.10	2.8
2	4.40 ± 0.08	4.20 ± 0.00	−4.6
3	4.54 ± 0.05	4.48 ± 0.00	−1.3
4	8.79 ± 0.21	8.95 ± 0.26	1.8
5	4.27 ± 0.08	4.18 ± 0.04	−2.2
6	7.11 ± 0.07	7.31 ± 0.18	2.8
7	3.14 ± 0.09	3.15 ± 0.13	0.1
8	10.59 ± 1.06	10.43 ± 0.29	−1.4
9	13.80 ± 0.18	14.47 ± 0.14	4.8
10	4.11 ± 0.17	4.03 ± 0.15	−1.9

[a] Average and standard deviation values ($n = 3$). [b] Relative deviation expressed in per cent. of the proposed method from the reference method.

The system is also versatile since other determinations can easily be carried out without physical reconfiguration of the manifold, except for the probable change of the detector. Moreover, it can easily be coupled to on-line monitoring.

Changes in the titration strategy are easily implemented by varying the titrator control parameters, thus enabling its adjustment to the accuracy of results intended.

The use of the Gran method allows a great saving of time since it is possible to use a reduced number of points to establish the one-side function.

The applicability of the proposed system to chloride determination in bottled natural waters confirms that the automatic flow titrator could represent an advantageous alternative to either batch or flow titration systems.

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