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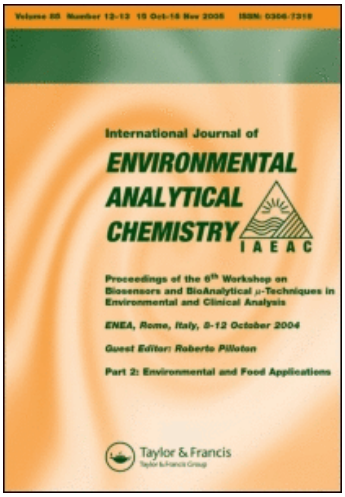

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OXIDABILITY DETERMINATION IN WASTE WATERS USING AN AUTOMATIC TITRATOR BASED ON A MULTICOMMUTATED UNSEGMENTED FLOW SYSTEM

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The automatic titrator based on a multicommutated unsegmented flow system was applied to redox titrations and used for oxidability determination in waters analysis. This automatic titrator allows the attainment of complete titration curves, being the determination of titrand concentration performed without requiring any prior calibration. After sample treatment (oxidation step), the oxidability determination in waste water samples was accomplished by the automatic flow titrator (titration step). Repeated determinations of standard solutions gave a 3.5% RSD (n=10, 0.010*M*) for repeatability and a 3.2% RSD (n=2, 0.057*M*) for reproducibility. Samples results (n=9) were in good agreement (*t*-test) with those obtained with a reference procedure.

Keywords: Multicommutated flow system; automatic flow titrator; oxidability; waste water; spectrophotometry

INTRODUCTION

The growing population and the increment in agricultural and industrial activities are endangering water quality calling for new monitoring methodologies for the control of natural and residual water quality[1–4].

One of the parameters used for water monitoring is oxidability that is related to the chemical oxygen demand and gives an indirect measure of the quantity of organic material present in water. The reference methodology[5] for the oxidability determination is based on the organic material oxidation, in acid medium, followed by titration. It is a manual time-consuming method that provides results

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dependent on the operator skills and, thus, being a limitation for routine analyses of laboratories responsible for the effluents control.

Several flow-based systems dealing with the development of automatic methods for organic material determination (chemical oxygen demand, i.e. COD) have been proposed[6–11]. Potassium dichromate[7,10] and potassium permanganate[6,8,9] in acid medium or cerium sulphate[11] with waterbath[6–9] or oil-bath[11] heating or assisted by microwaves[10] and with spectrophotometric detection[6–11] were used as oxidizing agents. All these methods are based on measurements carried out with different COD standard compounds (glucose, potassium hydrogenphthalate, sodium oxalate, sodium salicylate, sodium acetate, L-glutamic acid and lactose) to attain the sample results.

The present work intends to perform the titration step of the reference methodologies for the organic material determination (COD or oxidability) by an automatic titrator based on a multicommutated unsegmented flow system[12], which does not require prior calibration. It can be very useful to perform the titration step in the reference procedure for the oxidability or COD determination, making the whole procedure less tedious, or it can be easily coupled to flow systems[6–11] that perform the oxidation step of the organic material, making the whole procedure completely automatic but without the need for adequate standards.

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In this work the oxidability determination in waste water samples, after sample treatment (oxidation step), was accomplished by the automatic flow titrator (titration step). Potassium permanganate in acidic medium is used as oxidizing agent (oxidation step). After having added an excess of iron(II) to the sample, the titration step was performed using potassium permanganate as titrant and spectrophotometric detection[5].

The titration strategy is based on sequential introduction of increasing titrant and decreasing titrand volumes in a reactor (mixing chamber). This system enables to attain complete titration curves similar to those of batch titration systems, being the software developed able to control every step of the titration procedure, perform data acquisition and processing.

The model end-point time determination for each titrand standard concentration 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 because the determination of unknown titrand concentrations is carried out by an iterative procedure that based on the equations of developed model estimates the titrand concentration whose model end-point time corresponds to the experimental value.

The results obtained were reproducible and in good agreement with those given by a reference procedure.

THEORY

Titration strategy and equations of the theoretical model

The commutating devices used in the developed multicommutated flow system were valves (V)[12] that 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) (Figure 1). Considering that the flow-rate is constant throughout titration, the volume change can be determined from the time values.

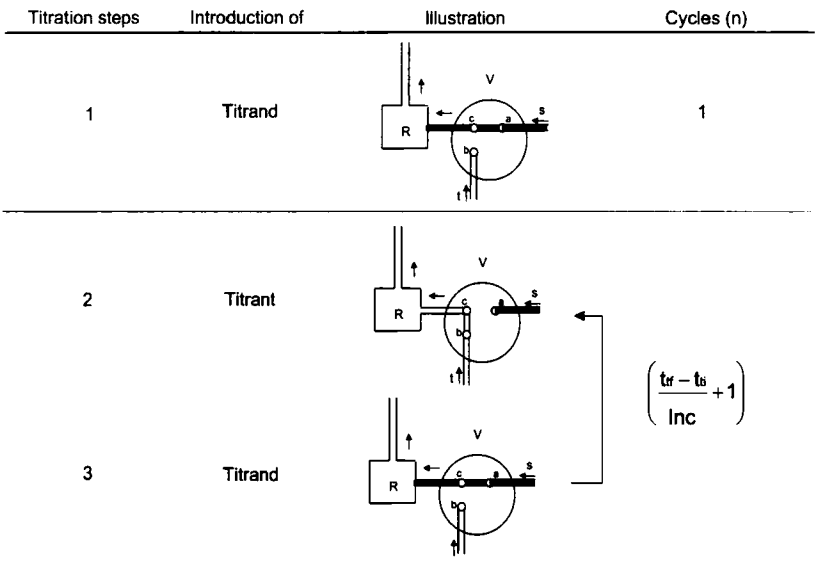

FIGURE 1 Schematic representation of the titration strategy. V: commutating valve; s: titrand solution; t: titrant solution; R: reactor (mixing chamber); a: titrand inlet; b: titrant inlet; c: outlet channel for both solutions (titrand and titrant); n cycles (the number of times a given titrant and titrand volume are introduced in the system)

The titration strategy proposed (Figures 1 and 2) is based on the sequential introduction of increasing titrant and decreasing titrand volumes in a reactor (a mixing chamber), after filling up with titrand, being these volumes determined by the valve commutation times.

Prior to titration, some parameters are set, such as initial (t_{ti}) and final (t_{tf}) titrant time, total time of each cycle (t_T) (kept constant throughout titration) and the titrant increment time (Inc). The titrand time (t_s) in each cycle is equal to the

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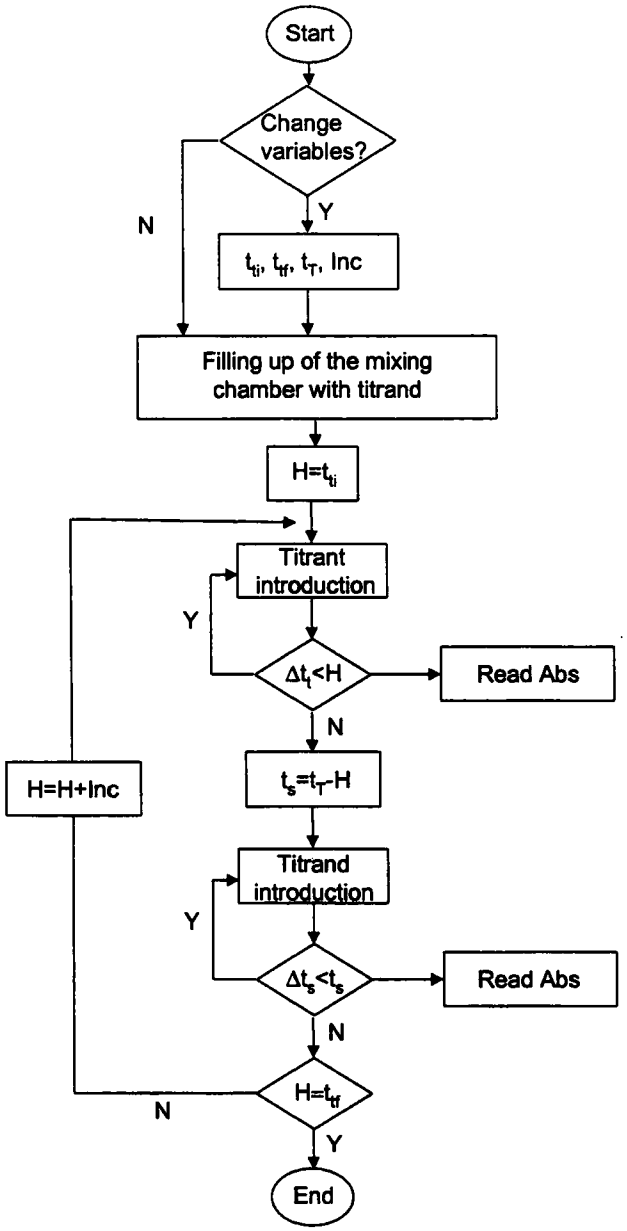

FIGURE 2 Algorithm flowchart of the titration. t_{ti} and t_{tf}: Initial and final titrant times, respectively; t_s: titrand time (corresponds to the remainder left after subtracting the titrant volume to the total volume of each cycle); t_T: total time of each cycle; Inc: titrant time increment

total time of each cycle subtracted by the titrant time of the present cycle ($t_s=t_T-t_t$).

First, the mixing chamber is filled up with titrand (Figure 1, step 1). Once titration is started the first titrant volume (corresponding to the first titrant time, named t_{ti}) is introduced in the mixing chamber (Figure 1, step 2). The initial titrant time (t_{ti}) is the same or higher than the lowest time allowing the introduction of an accurate volume (minimum volume) through the valve. The variation (reduction) of titrand concentration in the mixing chamber during introduction of titrant can be expressed[13,14] by:

$$C_s(t_x) = \left(-\frac{C^0{}_t}{n}\right) + \left(\frac{C^0{}_t}{n} + C_s(t_{y1})\right) \exp\left(-\frac{F}{V}(\Delta t_t)\right) \qquad \text{(eq. 1)}$$

where $C_s(t_x)$ is the variation of titrand concentration (mol/L) in the mixing chamber while titrant is being introduced; $C^0{}_t$ the titrant initial concentration (mol/L); $C_s(t_{y1})$ the titrand concentration (mol/L) 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); 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 + n titrant → products).

The next step corresponds to the introduction of a titrand volume (corresponding to a titrand time, named t_s) (Figure 1, step 3). The variation (increase) of titrand concentration over the introduction of titrand (increase usually smaller than the expected reduction derived from the introduction of titrant) into the mixing chamber can be expressed[13,14] by:

$$C_s(t_y) = C^0{}_s - (C^0{}_s - C_s(t_{x1})) \exp\left(-\frac{F}{V}(\Delta t_s)\right) \qquad \text{(eq. 2)}$$

where $C_s(t_y)$ is the variation of titrand concentration (mol/L) in the mixing chamber throughout titrand introduction; $C^0{}_s$, the titrand initial concentration (mol/L); $C_s(t_{x1})$, titrand concentration in the mixing chamber after introduction of titrant (just before the introduction of titrand); F, the flow-rate (L/s); V, the chamber volume (L) and (Δt_s), the time of titrand introduction into the mixing chamber.

The first cycle is hereby ended. This procedure is performed repeatedly (Figure 1, step 2 and 3), for n cycles, until the titrant time reaches the final time (t_{tf}). The titrant volumes introduced in the mixing chamber are higher and higher (by a fixed increment) and the titrand ones lower and lower, thus a complete titration curve being obtained. Throughout 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.

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At the end-point time the titrand concentration in the mixing chamber could be considered null ($C_s(t_x)=0$). This occurs during the introduction of titrant and thus at the model end-point time (t) eq. 1 becomes:

$$t = \frac{V}{F} \ln \left[1 + n \frac{C_s(t_y)}{C^0_t} \right] \qquad \text{(eq. 3)}$$

where t is the model end-point time (s); V, the chamber volume (L); F, the flow-rate (L/s); n, the stoichiometric coefficient of the reaction (titrand + n titrant $\rightarrow$ products); $C_s(t_y)$, the titrand concentration (mol/L) in the mixing chamber just before the titrant introduction and C^0_t, the titrant initial concentration (mol/L).

The data obtained from the titration process is 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.

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Determination of model end-point time and titrand concentration

The determination of the model end-point time for each titrand standard concentration is based on eq. 1 (during titrant introduction) and eq. 2 (during titrand introduction), and corresponds to the titration time spent until the titrand excess swifts to titrant excess (eq. 3). The model end-point time will correspond to the titration time when a constant excess of titrant is attained because there is the possibility of briefly occurring an excess of titrant that is consumed by the next introduction of titrand. The determination of titrand unknown concentration (Figure 3) is carried out by an iterative procedure that based on the equations (eqs. 1 and 2) of the theoretical model estimates the titrand concentration the model end-point time (t) of which corresponds to the experimental value (t_E). Therefore, the necessary subroutine allowing the determination of titrand concentration was implemented (Figure 3). This subroutine determines the model end-point time corresponding to a simulated concentration interval. For the calculation, parameters like titrant initial concentration (C^0_t), mixing chamber volume (V), flow-rate (F), initial (t_{ti}) and final (t_{tf}) titrant time, total time of each cycle (t_T), titrant time increment (Inc) and stoichiometric coefficient of the reaction (n) must be known. Also parameters like simulated theoretical initial concentration (C) and concentration increment (C_{Inc}) must be chosen. After each assessment, the model end-point time obtained (t) and the experimental one (t_E) are compared. If the value found is lower than the experimental one ($t<t_E$), the system moves on to the next concentration ($C_s=C_s+C_{inc}$) for the assessment of the new model end-point time. Only when the time assessed matches the experi-

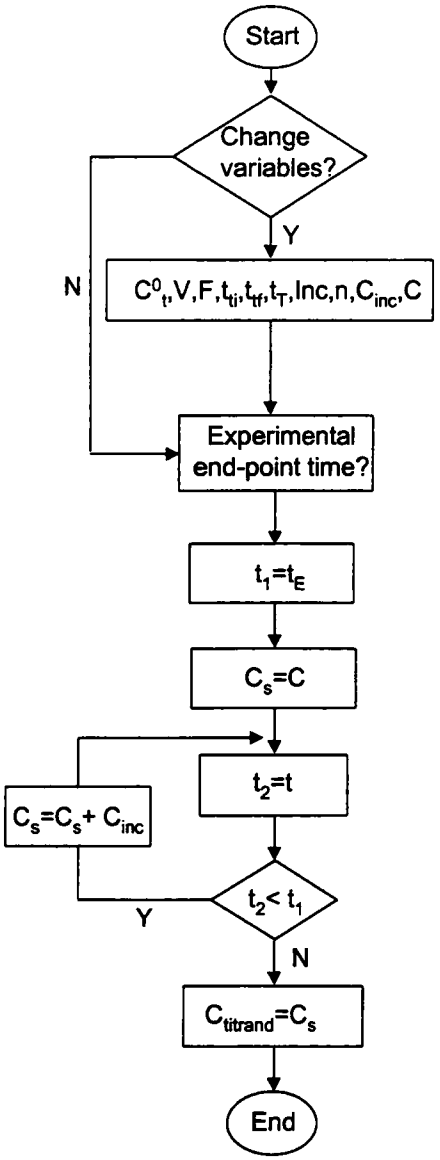

FIGURE 3 Algorithm flowchart for the determination of titrand concentration. C^0_t: titrant initial concentration; V: chamber volume; F: flow-rate; t_{ti} and t_{tf}: initial and final titrant time, respectively; t_T: total time of each cycle; n: stoichiometric coefficient of the reaction; C_{inc}: concentration increment value; C: theoretical initial concentration; t_1: experimental end-point time; t_2: model end-point time and $C_{titrand}$: titrand concentration

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mental value ($t=t_E$) the titrand concentration corresponds to model one ($C_{titrand}=C_s$).

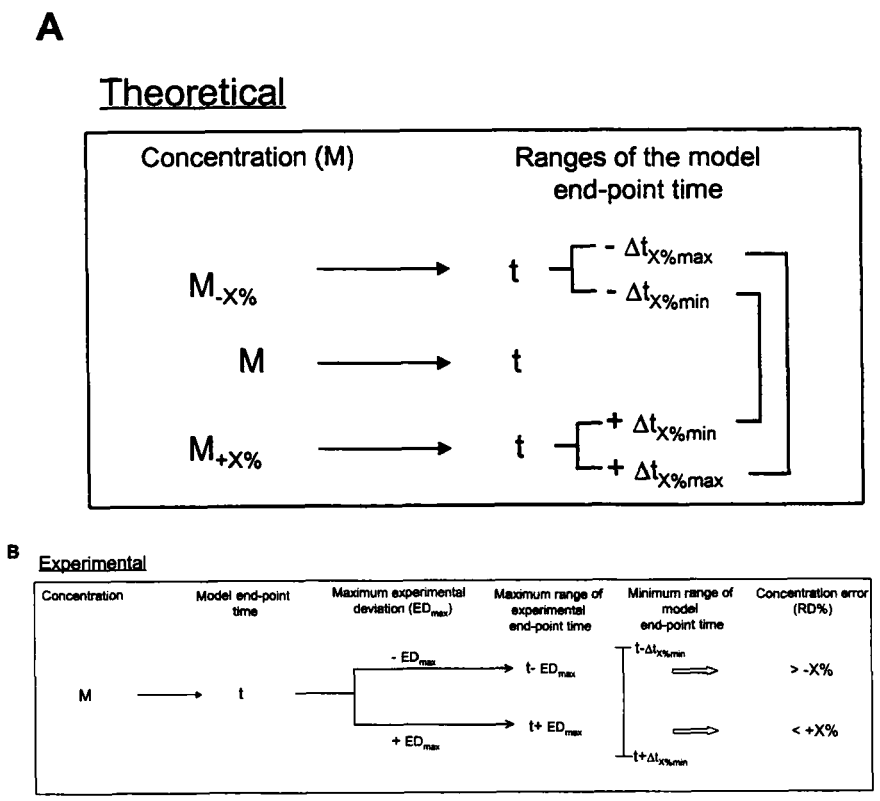

FIGURE 4 (A) Model end-point time ranges corresponding to a concentration interval of ±X% for a solution of concentration M; (B) Experimental end-point time range expected for the titration of the same solution and comparison with the model time interval that allows to obtain a concentration error (RD) less than X%

Accuracy model

The optimisation of the automatic titrator system is mainly dependent on the accuracy required for the results. Assessing the possibility to determine a titrand concentration with a maximum error of ±X% (relative deviation, i.e. RD) requires the attainment of the model time range of that error (Figure 4A) as well as if the experimental values (values range) are within that range (Figure 4B). To find out the model time range of the error (±X%) it is initially necessary to calcu-

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late, based on the theoretical model previously referred (eqs. 1 and 2), the model end-point times expected for concentrations differing 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 standard deviation of the time differences). Only concentrations differing X% from each other and with different end-point times, named titratable concentrations, are considered in this calculus (concentrations differing X% with the same end-point time are excluded and cannot be titrated by the system). The model 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, where t is the model end-point time for the concentration *M*) (Figure 4A).

The experimental end-point times (values range) obtained when the same solution (concentration *M*) is titrated must be within the minimum model 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 X% from each other, to assure errors less than X% (Figure 4B).

The accuracy of the experimental values was evaluated by titration of several standard solutions and subsequent comparison of the different end-point times obtained with those expected by the theoretical model. We name the differences found between model and experimental times experimental deviations (ED, meaning the expected deviations relative to the model time value). The determination of the whole experimental time range expected when any concentration is titrated (this is the example with the *M* value) is carried out using the highest experimental deviation (ED_{max}) of the experimental deviation range ($ED \pm \sigma_{ED}$) obtained with the standard solutions, being the time interval limits ($t-ED_{max}$ and $t+ED_{max}$) calculated from the expected model end-point value (t) (Figure 4B).

In order to obtain relative errors less than X%, the whole experimental time range expected for any concentration must be within the minimum model time range of the error (meaning that the ED_{max} value has to be equal or less than the $\Delta t_{X\%min}$ value) (Figure 4B).

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.

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A potassium permanganate solution prepared from the standard by dilution with deionised water was used as titrant and oxidizing agent. The acid medium was obtained using sulphuric acid.

The iron(II) solutions (0.0084 – 0.34 *M*) prepared from ammonium iron(II) sulphate were standardised by titration with potassium permanganate, which was also used for flow titrations.

The samples were prepared (oxidation step) by the reference procedure[5].

Instrumentation and apparatus

Omnifit Teflon tubing (0.8 mm i.d.) and connectors were used for manifold conduits. A Perspex mixing chamber with a magnetic stirrer was used as reactor.

A Valco two-position air actuated valve (Valco Instruments Co. Inc.) controlled by a Valco digital valve interface (DIV), actuated by TTL signals, was selected as switching device. This valve presented four ports but only three were used so that the same outlet channel was operated. The minimum volume introduced in the system in an accurate and reproducible manner was 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 introduced at different commutation times) were evaluated for more than 12 months and they were found stable (RD ≤ 5%).

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 JENWAY 6300 spectrophotometer, with a flow-through cell (10 mm light path, 8-μL optical volume), was used as detector.

The titration curves of the prior trials were recorded using a Kipp & Zonen recorder.

RESULTS AND DISCUSSION

Flow system manifold

A schematic representation of the flow system developed is shown in Figure 5. An automatic burette placed at the end line of the system was used to keep a con-

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stant flow-rate. A pneumatic actuated valve was used for the introduction of different titrand and titrant volumes in the system and the commutation times were controlled by a microcomputer (occurring a direct relationship between commutation times and volumes). The different titrand and titrant volumes were sequentially introduced in the mixing chamber resulting in their immediate mixing. The monitoring of the analytical signal was accomplished spectrophotometricly at 525 nm. The path lengths between the valve and the mixing chamber and between the latter and the detector were kept at the minimum value.

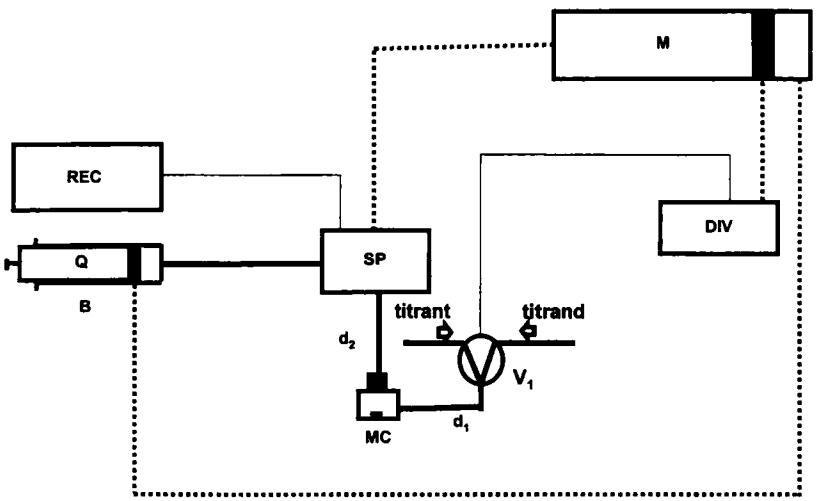

FIGURE 5 Schematic representation of the manifold developed. B: burette aspirating pump; SP: spectrophotometer; REC: recorder; MC: mixing chamber (370 μL); Q: flow-rate (0.46 mL/min); DIV: Valco digital valve interface; M: microcomputer; V_1: commutating valve; d_1: path length between the valve and the mixing chamber (4 cm); d_2: path length between the mixing chamber and the spectrophotometer (20 cm)

System optimisation

For the evaluation and optimisation of the automatic flow titrator different concentrations of iron(II) standard solutions were titrated with potassium permanganate (Figure 6). The end-point time occurred at the intersection of the two straight lines (before and after the end-point). The detector reaching time previously evaluated and used in the model was 20s.

The accuracy evaluation of the titration system was based on the accuracy model already described. The accuracy intended for the results was less than 5%

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(relative deviation) when compared with those obtained by the reference procedure.

TABLE I Titrant and titrand times and number of cycles needed to perform titrations with different initial (t_{ti}) and final (t_{tf}) titrant times and different titrant time increment (Inc)

	Initial titrant time (s) : Final titrant time (s)					
	0.3 : 7.7				1.6 : 6.4	
	Titrant increment (s)				Titrant increment (s)	
	0.1		0.2		0.1	
Cycle (n)	Titrant time (s)	Titrand time (s)	Titrant time (s)	Titrand time (s)	Titrant time (s)	Titrand time (s)
1	0.3	7.7	0.3	7.7	1.6	6.4
2	0.4	7.6	0.5	7.5	1.7	6.3
3	0.5	7.5	0.7	7.3	1.8	6.2
4	0.6	7.4	0.9	7.1	1.9	6.1
5	0.7	7.3	1.1	6.9	2.0	6.0
6	0.8	7.2	1.3	6.7	2.1	5.9
7	0.9	7.1	1.5	6.5	2.2	5.8
8	1	7	1.7	6.3	2.3	5.7
.	↓	↓	↓	↓	↓	↓
38			7.7	0.3		
.					↓	↓
49					6.4	1.6
.	↓	↓				
75	7.7	0.3				

The t_{ti}, t_{tf}, t_T and Inc values selected for the determination of the $\Delta t_{5\%}$ value and respective standard deviation ($\pm\sigma\Delta t_{5\%}$) were 0.3s (lowest commutation time for a 0.46 mL/min flow-rate), 7.7s, 8s and 0.1s, respectively (Table I). The value of the stoichiometric coefficient of the reaction (n) equals 0.2. The $\Delta t_{5\%}\pm\sigma\Delta t_{5\%}$ value was assessed using only the titratable concentrations (concentrations differing 5% from each other and with different end-point times) that under the selected conditions corresponded to concentrations with end-point times from 130s to 600s. Working under these conditions, the system run determinations at a concentration ratio of 40 (ratio between the higher and the lowest limit of the concentration interval). The $\Delta t_{5\%}\pm\sigma\Delta t_{5\%}$ value estimated was 6.5±2.5s (Table II), using a concentration of 0.0089 *M* for the titrant solution and of about 0.0084 M up to 0.34 *M* for titrand solutions. Hence, the $\Delta t_{5\%min}$ value accomplished was 4s.

For experimental purposes, different (n=9) iron(II) standard solutions in concentrations ranging from 0.0097 *M* to 0.32 *M* were titrated for several days (n=2) so as to determine the $ED\pm\sigma_{ED}$ (average and standard deviation of the experimental deviation, respectively) value, which was found to be –0.3s±4.1s (Table III).

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In order to obtain relative deviations less than 5%, the ED_{max} value (about 4s) has to be equal or less than the $\Delta t_{5\%min}$ (4s), what does usually occur. Therefore, under these conditions the system works according to the parameter previously set (RD less than 5%) (Table III).

TABLE II Theoretical variation of $\Delta t_{X\%}$ values for concentrations differing (CD) by 5%, 10% and 15% and for different titrant ($t_{ti} - t_{tf}$) and titrand ($t_{si} - t_{sf}$) time ranges and titrant time increment (Inc)

		CD=5%		*CD=10%*		*CD=15%*	
$t_{ti} - t_{tf}$[a] (s) $t_{si} - t_{sf}$[b] (s)	Inc (s)	$\Delta t_{5\%}$[c] (s)	$\Delta t_{5\%min}$ (s)	$\Delta t_{10\%}$[c] (s)	$\Delta t_{10\%min}$ (s)	$\Delta t_{15\%}$[c] (s)	$\Delta t_{15\%min}$ (s)
0.3 – 7.7	0.1	6.5±2.5	4	10.8±4.3	6.5	15.4±5.8	9.6
7.7 – 0.3	0.2	3.5±2.5	1	6.4±2.5	3.9	9.0±3.4	5.6
1.6 – 6.4 6.4 – 1.6	0.1	7±2.4	4.6	12.7±3.7	9	17.7±5.5	12.2

a. t_{ti}: initial titrant time and t_{tf}: final titrant time.
b. t_{si}: initial titrand time and t_{sf}: final titrand time.
c. Average and standard deviation.

TABLE III Maximum experimental deviation (ED_{max}), maximum expected result error MERE (RD%) and total titration time obtained with different titrant ($t_{ti} - t_{tf}$) and titrand ($t_{si} - t_{sf}$) time ranges and titrant time increment (Inc)

$t_{si} - t_{sf}$ [a] (s) $t_{ti} - t_{tf}$ [b] (s)	*Inc (s)*	*EDmax (s)*	*MERE (RD%)*	*Total titration time (s)*
0.3–7.7	0.1	4	±5%	600
7.7–0.3	0.2	5.5	±15%	304
1.6–6.4 6.4–1.6	0.1	5	±5%	392

a. t_{si}: initial titrand time and t_{sf}: final titrand time.
b. t_{ti}: initial titrant time and t_{tf}: final titrant time.

The theoretical determination of the $\Delta t_{\%}$ value and the titratable concentrations range when the relative deviations allowed diverged from the 5% was likewise performed. Relative deviations of 10% (the t_{ti}, t_{tf}, t_T and Inc times being equal to 0.3s, 7.7s, 8s and 0.1s, respectively) corresponded to a $\Delta t_{10\%}$ value of 10.8±4.3s ($\Delta t_{10\%min}$ equal to 6.5s) (Table II) and to a titratable concentrations ratio of about 100 (ranging from 0.0029 *M* to 0.32 *M* when the titrant presented a 0.0089 *M* concentration); similarly, relative deviations of 15% (the t_{ti}, t_{tf} and Inc times being equal to 0.3s, 7.7s and 0.1s, respectively) corresponded to a $\Delta t_{15\%}$ value of 15.4±5.8s ($\Delta t_{15\%min}$ equal to 9.6s) (Table II) and to a titratable concentration

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ratio of about 160 (ranging from 0.002 *M* to 0.32 *M* when the titrant presented a 0.0089 *M* concentration).

As the results relative deviation increased (10% or 15%), the ratio of titratable concentrations also increased due to the different model end-point times found for lower and lower concentrations. The $\Delta t_{\%}$ values (10% and 15%) increased as well because the model end-point times of concentrations varying 10% or 15% from each other were much more divergent.

Titrant time increment vs total titration time

Aiming the reduction of the total titration time (from 600s to 304s) but with the same accuracy of the results (RD less than 5%), the experimental deviation was assessed for a titrant time increment of 0.2s (using the same initial and end titrant time, total time of each cycle and titrant concentration already used, i.e. 0.3s, 7.7s, 8s and 0.0089 *M*, respectively) (Table I).

According to the theoretical model, the $\Delta t_{5\%}$ value decreased with the titrant time increment increase because of the smaller difference between end-point times that distinguish the concentrations varying 5% from each other. The value found for $\Delta t_{5\%}$ was 3.5±2.5s (Table II). The increase of the titrant time increment promoted also the decrease of the range of titratable concentrations, the ratio of this being about 10 (concentration from 0.018 *M* to 0.18 *M*, with a titrant concentration of 0.0089 *M*).

The experimental deviation (ED) found with five iron(II) (0.020 *M* – 0.11 *M*) standard solution was −1.3±4.2s. The ED_{max} value (about 5.5s) was higher than the $\Delta t_{5\%min}$ value (1s) and, therefore, some results presented higher than 5% deviation when an increment of 0.2s was used. In some cases, the results present errors (relative deviation) close to the 15% since the experimental deviation presents an ED_{max} value of $\Delta t_{15\%min}$ (Tables II and III).

Initial and final titrant time vs total titration time and titratable concentration

Reducing the interval between the initial and final titrant time (keeping the total time of each cycle and the titrant time increment constant, i.e. 8s and 0.1s, respectively) causes the titratable concentrations to diminish as well as the total titration time, though the $\Delta t_{5\%}$value is kept constant. Therefore, using a titrant time of 1.6s (t_{ti}) and 6.4s (t_{tf}), a titrant time increment of 0.1s, a total time of each cycle of 8s and a titrant concentration of 0.0089 *M*, the range of titratable concentrations (with end-point titration time higher than 90s) was 0.013 *M* – 0.11 *M* (concentration ratio of about 10) and the total titration time is 392s. The $\Delta t_{5\%}$ value is 7±2.4s (similarly to the $\Delta t_{5\%}$ value found when the t_{ti}, t_{tf} and t_T times were 0.3s, 7.7s and 8s, respectively) (Table II).

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The experimental deviation determined with a set of seven iron(II) standard solutions (0.03 *M* -0.10 *M*) on different days (n=2) was −1.6±3.4s. The ED_{max} value (about 5s) (Table III) is nearly the same as the $\Delta t_{5\%min}$ value (4.6s) shown in Table II. Hence, the results obtained hereby will present relative deviations less than 5%.

Mixing chamber volume vs accuracy

Theoretically, the influence of the mixing chamber volume in the model end-point times is about 8s for variations of the mixing chamber volume of about 100 μL. Therefore, slight changes on the mixing chamber volume (determined by the fill-up time at a constant flow-rate) do not result in significant errors when the end-point times are evaluated.

Experimentally, the effect of the chamber volume on the results attained was also evaluated. The titration of one standard solution (0.011 *M*) using titrant times ranging from 1.6s (t_{ti}) to 6.4s (t_{tf}) and a titrant time increment of 0.1s but with different chamber volumes (284 μL e 370 μL) presented similar experimental deviations (-3.9s and − 4.7s, for 284 μL and 370 μL chamber volumes, respectively). From this it can be concluded that the accuracy of the results was quite independent of the chamber volume used.

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Evaluation of the automatic flow titrator

Given the purpose intended (relative deviations less than 5% comparing to the reference procedure), the conditions selected were titrant time increment of 0.1s, total time of each cycle of 8s and titrant times of 0.3s (t_{ti}) and 7.7s (t_{tf}) or 1.6s (t_{ti}) and 6.4s (t_{tf}).

Using standard solutions and operating the titrator system under the selected conditions, the effectiveness of the theoretical model, repeatability, reproducibility and accuracy were evaluated.

Effectiveness of the theoretical model

The effectiveness of the theoretical model was proved by comparing the experimental end-point times attained by titration of several iron(II) solutions (0.009 *M* - 0.32 *M*) with the model end-point times predicted by the theoretical model.

Studying the correlation of experimental and model end-point times showed that there was a good agreement (slope 1.0095, intercept −3.3846 and R^2=0.9997) for n=14.

The agreement between both values was assessed by the Student paired t-test, in which the t-value estimated (0.086) was lower than the tabled one (2.16), for a confidence level of 95% (n=14).

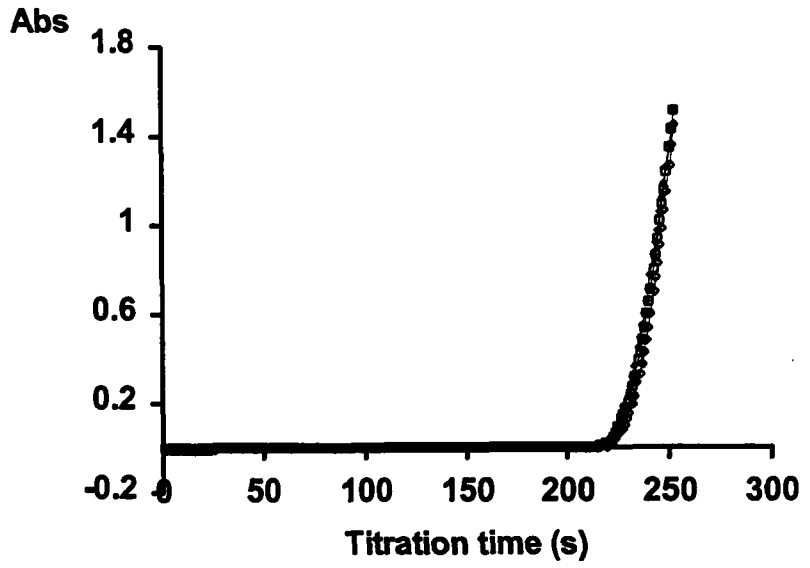

FIGURE 6 Sample titration curves (n=3)

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

Repeatability, reproducibility and accuracy

The repeatability was assessed by performing replicate titrations (n=10) of an iron(II) standard solution (0.01 *M*). A relative standard deviation (RSD) of 3.5% in the concentration values was obtained.

The reproducibility was attained by titration of an iron(II) standard solution (0.057 *M*) on different days (n=2), providing a relative standard deviation (RSD) of 3.2% in concentration values.

The accuracy was evaluated by comparing the concentration results of different iron(II) standard solutions (0.009 *M* - 0.32 *M*) accomplished with the automatic flow titrator and with the reference procedure. The correlation studies of the results given by the proposed and reference procedure showed that there was

a good agreement (the slope was 1.008764, the intercept 0.000074 and R^2=0.99964), for n=14.

Oxidability determination in waste water samples

The oxidation step was carried out by the reference procedure[5], in acid medium, with permanganate. After having added an excess of iron(II) (0.3 *M*), the volume was made up to 250 mL with deionised water. The amount of iron(II) added must be as much as to assure its final concentration within the titratable concentrations range. This volume was partly titrated in the flow by the automatic flow titrator and the remainder titrated manually according to the reference method[5], using the permanganate solution as titrant.

The titration with the automatic flow titrator of the excess of iron(II) present in the samples (Figure 6) was performed under the working conditions already referred (titrant time increment of 0.1s, total time of each cycle of 8s and titrant times of 0.3s (t_{ti}) and 7.7s (t_{tf})).

The results from the oxidability determination in waste water samples by the proposed method and by the reference method were compared by a relative deviation (in percentage) and shown in Table IV. The agreement between both values was also assessed by the Student paired t-test, in which the t-value estimated (1.25) was lower than the tabled one (2.31), for a confidence level of 95% (n=9).

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TABLE IV Results obtained in the oxidability determination (mg $O_2 x L^{-1}$) in waste waters, by the proposed method and by the reference method

Sample	*Reference method*[a]	*Proposed method*[a]	*RD(%)*[b]
1	2033.3±184.8	1886.7±4.6	−7.2
2	1089.3±166.5	1156.0±56.6	6.1
3	302.7±23.1	316.0±0.0	4.4
4	1471.2±83.1	1383.7±10.3	−5.9
5	1230.9±90.5	1155.2±18.1	−6.2
6	1158.4±135.8	1150±11.3	−0.7
7	1190.4±90.5	1159±1.8	−2.6
8	1371.2±11.3	1273±9.2	−7.2
9	1204.8±8.3	1283±0.0	6.5

a. Average and standard deviation values (n=3).
b. Relative deviation expressed in percentage of the proposed method to the reference method.

CONCLUSIONS

The automatic flow titrator presented proved to be suitable for carrying out under flow conditions the titration step of the oxidability determination in waste waters. This automatic flow titrator does not require any calibration step; it can be very useful to perform the titration step in the reference procedure for the oxidability or COD determination, making the whole procedure less tedious, or it can be easily coupled to flow systems that perform the oxidation step of the organic material, making the whole procedure completely automatic but without the need of adequate standards. The system proposed is quite simple since it is basically made of a valve (two independent inlets for the titrand and titrant, respectively, and a common outlet), a mixing chamber and a pump to keep a constant flow-rate. The coupling of the automatic flow titrator to any other system can be made through the sample inlet channel.

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