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Process systems engineering approaches to speed-up the auto-titrator operations

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Abstract−Acid-base titration is widely used in the fields of chemical engineering, environmental engineering, agriculture, and medical science. The auto-titrator is a commercial apparatus that carries out the titration operation automatically and provides equivalence point data. For some test samples and operating conditions, titration operations require up to 5 minutes. Here, we propose a method to reduce this operation time. For this, process systems engineering approaches such as alternative dosing of titrating and sample solutions, reducing sensor time-constant with a lead-lag filter and parameter identification technique have been applied. Simulations and experimental results with test equipment for auto-titration show the performance of the proposed method.

Key words: Auto-titrator, pH, Equivalence Point, Titration Curve

INTRODUCTION

Acid-base titration is an operation to find the equivalence point where pH value changes sharply when a titrating reagent is added gradually to a test sample. It can analyze concentrations in solutions, extents of textile weight losses and qualities of foods. The auto-titrator is a commercial apparatus that carries out the titration operation automatically and provides the equivalence data.

A typical auto-titrator [1] consists of a syringe pump, pH sensor, titrating reactor with a magnetic stirrer and a control computer. The syringe pump can dose the titrating reagent to the titrating reactor in micro-liter accuracy. For each dosing of the titrating reagent, the pH value in the titrating reactor is measured. The points that the slopes of pH values show local maximum are the equivalence points. The auto-titrator reports them. For some test samples and operating conditions, titration operations require around 5 minutes. Here, we propose a method to reduce this operation time.

For an accurate equivalence point, the amount of each dosing should be small near the equivalence point. A smaller dosing amount results in a large number of dosings, causing a long operation time. For a fast titration operation, a large amount of dosing at the initial part of titration and a small amount of dosing near the equivalence point are needed. However, the time to switch from a large amount of dosing to a small amount of dosing is not known in advance. For this, several methods adjusting the dosing amount adaptively have been suggested [1]. However, their performance is highly dependent on test samples. A complete solution for this is to use two syringe pumps with two titrating reagents of acid and base. However, one additional syringe pump increases the cost of the auto-titrator and causes additional maintenance problems. We propose a method to mimic this two syringe pump system without an additional syringe pump. Initially, titration starts with a large amount of each dosing. When it passes the equivalence point, a given amount of the sample solution is added. Then the titration operation resumes with a smaller amount of dosing. An accurate equivalence point can be obtained without spending time at the initial stage of titration [2].

Secondly, the pH sensor dynamics hinders fast dosing. Hence the titration time can be reduced if the pH sensor dynamics is made to be fast. There is a limit in forcing the dynamics of glass pH electrode to be fast by reducing the width of glass membrane. Instead, we accelerate the speed of the pH sensor by software. For this, we investigate the dynamic model of glass pH electrode. Applying inverse of the model of pH electrode dynamics, we speed up the pH sensor dynamics, resulting in a fast titration operation.

Finally, a physico-chemical model for the titration [3,4] is applied to find the equivalence point more accurately. The model proposed by Wright and Kravaris [4] is very effective in describing the pH system and is widely used for pH control systems [5]. A 2-parameter nonlinear model is used here to enhance the accuracy of equiva-

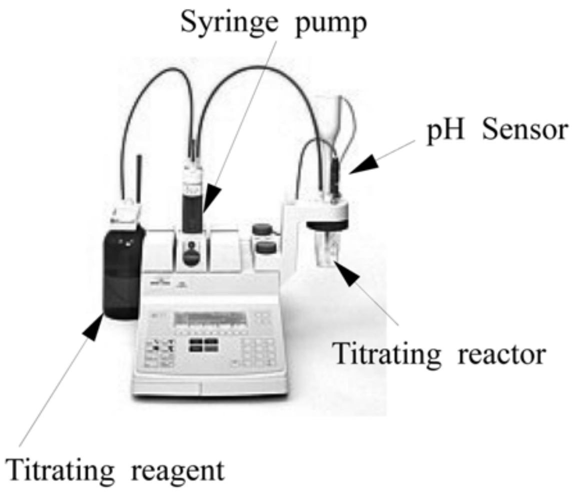

Fig. 1. A typical commercial auto-titrator.

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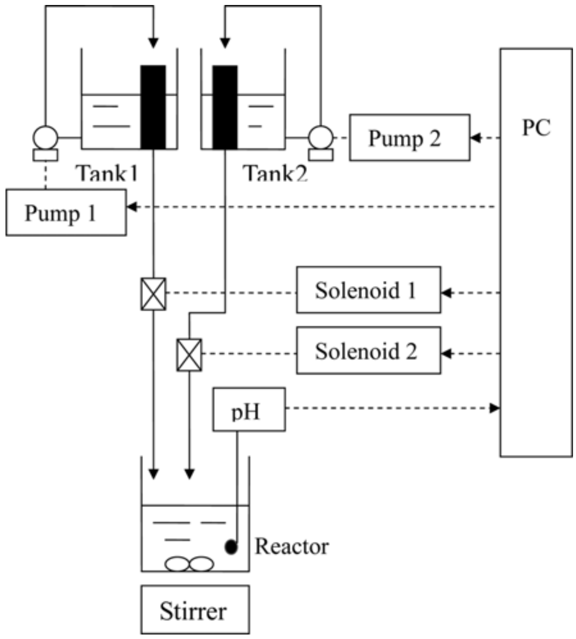

Fig. 2. A test system for the auto-titrator.

lence point. Linear least squares method is used to identify the 2-parameter model [6]. Simulations show that accuracy in finding the equivalence point can be increased considerably without decreasing the amount of each dosing further. It will reduce the dosing number and, consequently, the titration time.

The proposed method is tested by assembling equipment economically with recent minipumps and electronic instruments.

TEST EQUIPMENT

The test system for auto-titrator operation is shown in Fig. 2. Pump 1 pumps the titrating reagent in Tank 1 so that the liquid level in the shade pipe inside of Tank 1 is maintained to be constant. By activating Solenoid 1 during a given time period, we can add a given amount of the titrating reagent to the reactor. This dosing of titrating reagent may have errors in dosing amounts, compared to the syringe pump dosing used in the commercial auto-titrator. However, it will simulate the syringe pump operation economically. Pump 2 pumps the sample solution in Tank 2 and fills the shaded pipe inside of Tank 2. Then Pump 2 is turned off after the shaded pipe of Tank 2 is full. By activating the Solenoid 2, we can add a given amount of sample solution to the reactor. The glass pH sensor is used to measure the pH value in the reactor. A magnetic stirrer is used to mix solutions.

The pH sensor signal is buffered and amplified by the operational amplifier whose input bias current is in the range of pA. It is converted to digital signal through a 16 bit sigma-delta A/D converter. Sampling time is set to 50 milisecond.

METHODS TO SPEED-UP THE AUTO-TITRATOR OPERATION

1. Dosing Method

By adding a small amount of the titrating reagent in series, we can obtain the titrating curve and consequently the equivalence point by analyzing its slope. For each dosing of the titrating reagent, the pH value in the titrating reactor is measured. For an accurate equivalence point, the amount of each dosing should be small near the equivalence point. Smaller dosing results in a large number of dosings, causing a large operation time. To reduce this dosing number without sacrificing the titration accuracy, several methods adjusting the dosing amount adaptively have been suggested. However, their performance is highly dependent on test samples. A complete solution for this is to use two syringe pumps with two titrating reagents of acid and base. However, one additional syringe pump increases the cost of the auto-titrator and causes additional maintenance problems. Here, we propose a method to mimic this two syringe pump system without an additional syringe pump. Specifically, a method which adds a given amount of test sample when the amount of titrating reagent pass the equivalence point is proposed and its performance is tested.

The equivalence point is the point where the titration curve shows the peak slope. For a sample acid solution and a titrating base reagent, the equivalence point is such that

$$Fc_1 = uc_0 \tag{1}$$

where F is the amount of sample acid solution (L), c_1 is the concentration (mol/L), u is the amount of titrating base reagent (L) and c_0 is the concentration (mol/L), respectively. In Eq. (1), F and c_0 is known. From u* satisfying Eq. (1), which is found via the titration operation, we can find c_1.

When a constant amount of dosing of the base titrating reagent (Δu) is used, the number of total dosings ($n_{\Delta u}$) is

$$n_{\Delta u} = \text{int}(u/\Delta u) + 2 = \text{int}\left(\frac{Fc_1/c_0}{\Delta u}\right) + 2 \tag{2}$$

where int( ) denotes the truncated integer value. A smaller Δu for better estimation of the equivalence point increases the number of dosing.

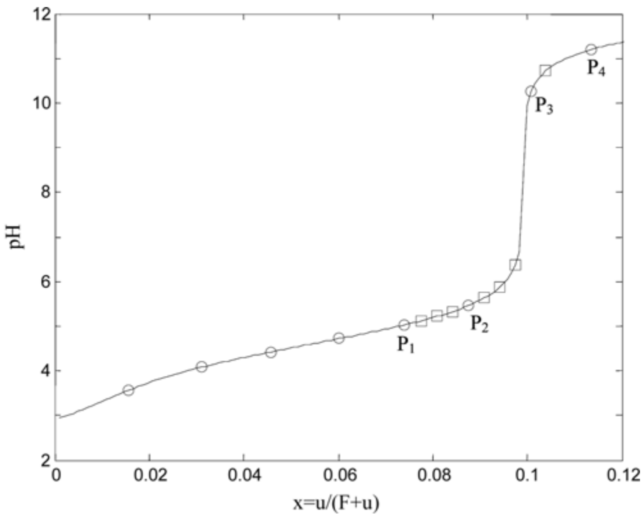

Fig. 3. A titration curve and the proposed dosing sequence (simulation). Sample solution: HCl (0.001 mol/L), acetic acid (0.008 mol/L, K_a=1.8×10^{-5}), and benzoic acid (0.002 mol/L, K_a=6.28×10^{-5}), titrating reagent: NaOH (0.1 mol/L).

Circular points in Fig. 3 are obtained by adding a given amount of titrating reagent in series. When P_4 in Fig. 3 is approached, we can see that the equivalence point is between P_1 and P_4. At P_4, we add a given amount of the sample solution (F_{add}) and a corresponding titrating reagent (u_{add}) simultaneously so that the titration status is returned to the point P_1:

$$\frac{u_{P1}}{F+u_{P1}}=\frac{u_{P1}+u_{add}}{F+F_{add}+u_{P1}+u_{add}} \tag{3}$$

where u_{P1} are the amount of titrating reagent at P_1. Then we resume the titration operation with a smaller amount of dosing (Δu_{new}) such that

$$\Delta u_{new}=\Delta u\frac{F+F_{add}}{4F} \tag{4}$$

Square points in Fig. 3 are obtained with adding this smaller amount of titrating reagent again.

The proposed method will reduce the number of dosings needed to obtain the equivalence point with a given estimation accuracy. The degree of reducing the dosing number is dependent on problems. The proposed method will be more effective for highly accurate estimation of the equivalence point. Fig. 4 shows a typical experimental result. Here, circular points are for the first dosing amount of titrating reagent and square points are for the new dosing amount.

2. pH Sensor Dynamics

The glass pH sensors have dynamics. For each dosing, we should wait for about several seconds until the pH measurements settle down. This transient dynamics is estimated and a method to speed-up this transient time is investigated. Reduction of this time directly reduces the total time of auto-titration.

The pH sensor dynamics are dependent on the glass pH electrode and the mixing characteristics of titrating reactor. The dynamics is obtained once for an auto-titrator system and can be used for subsequent operations. Fig. 5 shows the experimental transient responses of a glass pH electrode system. With buffer solutions of pH 4, 7 and 10, the transient responses according to changing buffer solutions are shown. Changes from pH 4 to 10 and 10 to 4 are scaled by half. We can see that very similar responses are obtained.

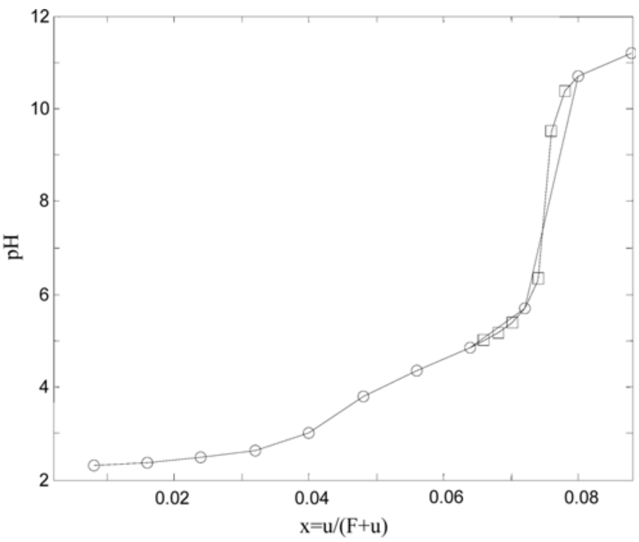

Fig. 4. A titration curve and the proposed dosing sequence (experimental result). Sample solution: HCl and acetic acid, titrating reagent: NaOH (0.1 mol/L).

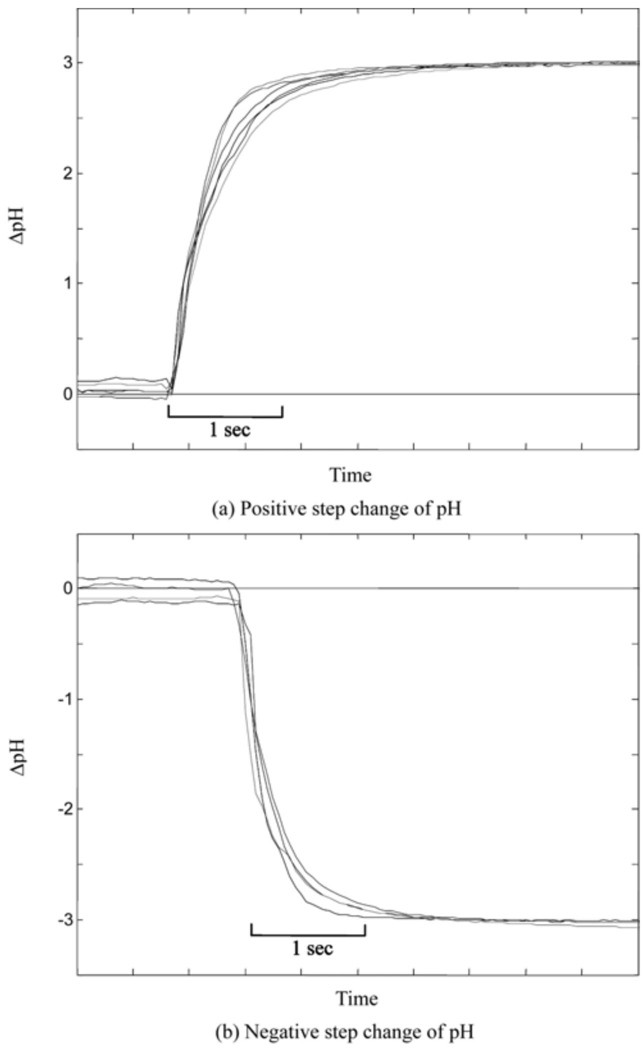

Fig. 5. Transient responses of a glass pH sensor (experimental results).

From these responses, we can obtain a time constant of this pH sensor of about 0.35 second. Since, the dynamics of the glass pH sensor system can be approximated by a transfer function of

$$G_{sensor}(s)\approx\frac{1}{0.35s+1} \tag{5}$$

Hence a filter

$$G_F(s)=\frac{0.35s+1}{0.1s+1} \tag{6}$$

can be used to increase the speed of transient response. Fig. 6 shows the performance of the filter in Eq. (6). Denominator in Eq. (6) is introduced to reduce noise effects of the pH sensor.

3. Parameterization of Titration Curve

Steady-state models for the acid-base reaction are well-established [3-6]. A model where a weak acid is titrated with a strong base is given as

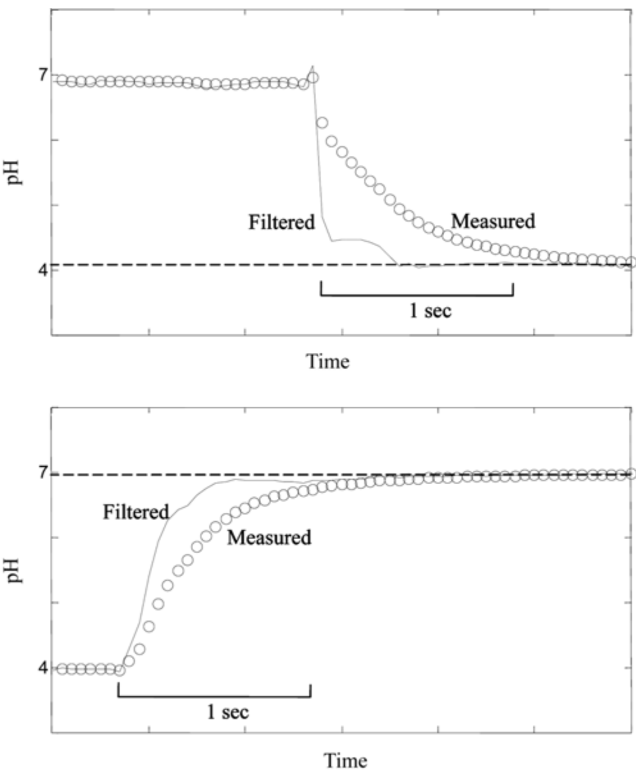

Fig. 6. Filtered transient responses of a glass pH sensor.

$$x=\frac{u}{F+u}=\frac{-\dfrac{c_1}{1+10^{-pH}/K_a}+10^{-pH}-\dfrac{K_w}{10^{-pH}}}{-\dfrac{c_1}{1+10^{-pH}/K_a}-c_0} \tag{7}$$

where K_w is the ion product of water (10^{-14}), c_0 is the concentration of the titrating reagent, c_1 and K_a are the unknown concentration and dissociation constant of the weak acid, respectively. Eq. (7) can be rearranged as

$$\left[\frac{1-x}{c_0x+10^{-pH}-\dfrac{K_w}{10^{-pH}}}-10^{\{7-pH\}}\right]\left[\begin{array}{c}c_1\\ \dfrac{10^{-7}}{K_a}\end{array}\right]=1 \tag{8}$$

This equation is linear for the unknown parameters of c_1 and $-10^{-7}/K_a$. Hence, we can apply the linear least squares method. Simulation results are shown in Figs. 7 and 8. Three data points where two points are below the equivalence point and one is over the equivalence point are used.

For the sample solution of Fig. 7, estimations are excellent. We can see that rather sparsely spaced data points (circle points in Fig. 7) provide very accurate estimate of the equivalence point. For the sample solution of Fig. 8, compared to that of Fig. 7, closer data points are needed to obtain estimates of the equivalence point. This is because the sample solution of Fig. 8 is hard to describe with the one weak acid model of Eq. (7). However, the proposed estimation is still effective because data points used to estimate the equivalence point will be much closer than those in Fig. 8.

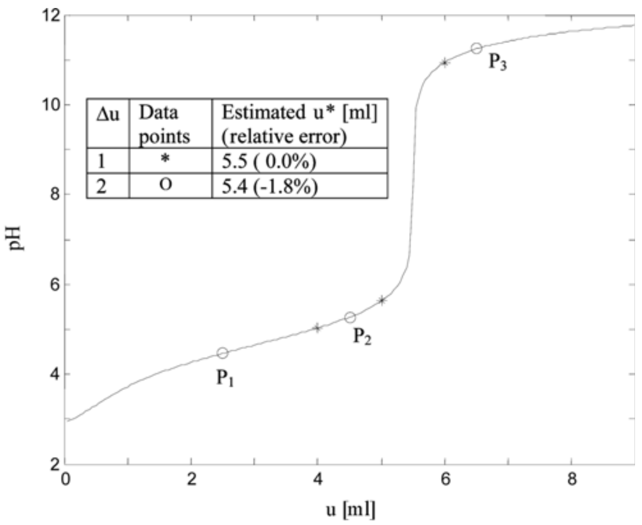

Fig. 7. Titration data points and estimations of the equivalence point with the physico-chemical model (simulation). Sample solution (50 ml): HCl (0.001 mol/L), acetic acid (0.008 mol/L, K_a=1.8×10^{-5}), and benzoic acid (0.002 mol/L, K_a=6.28×10^{-5}), titrating reagent: NaOH (0.1 mol/L).

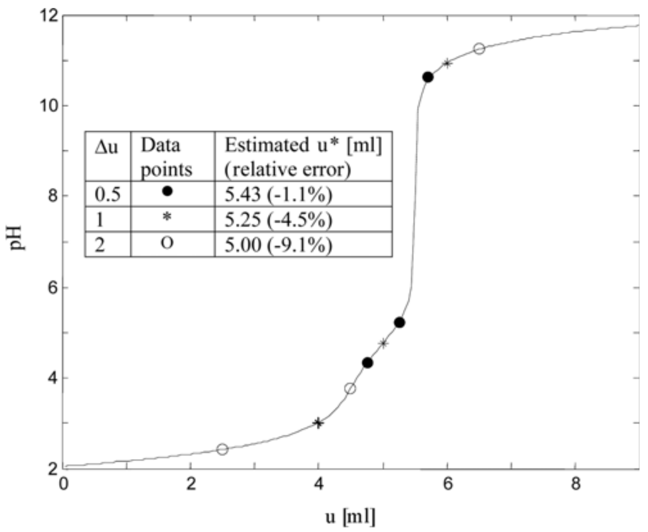

Fig. 8. Titration data points and estimations of the equivalence point with the physico-chemical model (simulation). Sample solution (50 ml): HCl (0.009 mol/L) and acetic acid (0.002 mol/L, K_a=1.8×10^{-5}), titrating reagent: NaOH (0.1 mol/L).

CONCLUSION

A method to reduce the time of auto-titrator operation is proposed. For this, process systems engineering approaches such as reducing sensor time-constant with a lead-lag filter, parameter identification and alternative dosing of titrating and sample solutions have been applied. The degree of operation time reduction is dependent on sample solutions and operation conditions. The proposed method is more effective when more accurate estimation of the equivalence point is needed. Auto-titrator operation times requiring up to 5 minutes will be reduced below 1 minute. With this method, auto-titrators can be used more efficiently.

A commercial auto-titrator does not provide a special mixing tank and just uses a small beaker with magnetic stirrer. Washing might be one of the reasons for this. However, mixing also affects the auto-titrator operations much. Study about better mixing will reduce the auto-titrator operation time considerably.

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