

# Diagnostics of the pH-meter State in Real Time

Dmitry I. Dikhno  
PJSC Acron  
Velikiy Novgorod, Russia  
ddikhno@yandex.ru

Victoria V. Kurkina<sup>1</sup>, Leon A. Rusinov<sup>2</sup>  
St. Petersburg State Institute of Technology (technical  
university)  
St. Petersburg, Russia  
victoria.kurkina@gmail.com<sup>1</sup>, lrusinov@yandex.ru<sup>2</sup>

**Abstract**— A method of real-time evaluation of the industrial pH-meter state by comparing the measured values of the hydrogen index and the flow rates ratio of reagents when the concentration of one of them changes is considered. The range of values of the hydrogen index is determined, in which the influence of changes in the concentration of the reagent has a slight effect on the accuracy of determining the pH meter state.

**Keywords**— the control of the pH-meter state; the titration curve analysis; link of the hydrogen index and flow rate of reactant

The need to measure the hydrogen index (hereinafter-pH) in industry is quite common, and usually requires the stabilization of pH at a given value. In this case, to maintain the pH at the specified values, the flow rate of the initial solution is needed to change. The least reliable element in the pH control circuit, as shown in [1], is the pH electrode of the pH meter. In practice, this is usually due to the drift of the pH meter calibration.

The offset of the pH meter calibration increases the difference between the true and measured pH values. At the same time, the target indexes of the technological process also deviate from the optimal [2]. Timely diagnosis of the pH meter can significantly improve the efficiency of the process.

At the same time, as shown in [1], the most significant source of data of the pH electrode state is the deviation of the ratio of the flow rates of reagents that affect the value of the hydrogen index (hereinafter-the specific flow rate), from the expected one at this pH value. The regulator maintains the set pH value by changing the specific flow rate.

In this case, when the pH meter calibration is shifted, the regulator will maintain the distorted pH value. Upon that the displacement of the measured pH relative to the true value will be manifested in the change of the specific flow rate. That is why the control of specific flow rate that is used in the method proposed in [1] to determine automatically the fact of possible displacement of the pH meter calibration.

The applicability of the proposed method was evaluated by the example of a continuous system in which the initial solution containing weak acid needs to be neutralized with a strong base [3].

The proposed method of assessing the pH meter is based on a comparison values of pH and specific flow rate. In this case,

a solution with a weak acid and a strong base is considered. The titration curve of the process is shown in Fig. 1.

It was assumed that both the composition and concentration of the reagents are constant. However, in practice, if the qualitative composition can be considered constant, the concentration of reagents may vary in a limited range. Usually this is due to one of the reagents, which is the result of chemical reactions that occurred at previous stages of the process.

At the same time, another reagent is usually a standard universal substance with a strictly regulated and controlled composition. We will consider the initial solution as a reagent with a non-permanent composition, and a strong base – a reagent with stable properties.

Fig. 2 shows the scheme of automation of the technological object. The regulator AC-3 regulates the pH according to the pH meter A-3, by changing the coefficient "K" in the block of flow rates ratio FY-1 of initial solution (flowmeter FT-1) and strong base (by flowmeter FT-2).

Flow rate of the initial solution is stabilized at the setpoint by controller FC-1 through valve FCV-1. The setpoint of the strong base flow rate are adjusted to reflect the coefficient "K" and stabilized by controller FFC-2 through valve FCV-2. Regulator TS-4 regulates the temperature (according to the thermometer TT-4) by changing the flow rate of the coolant through valve TCV-4.

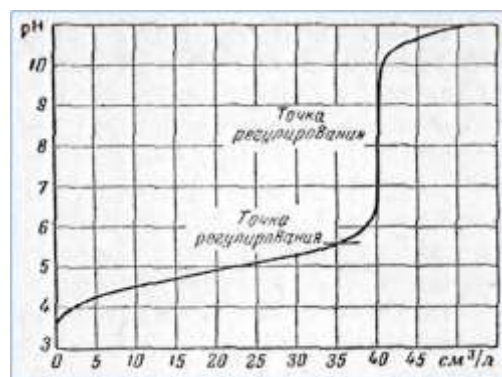


Fig. 1. Model titration curve

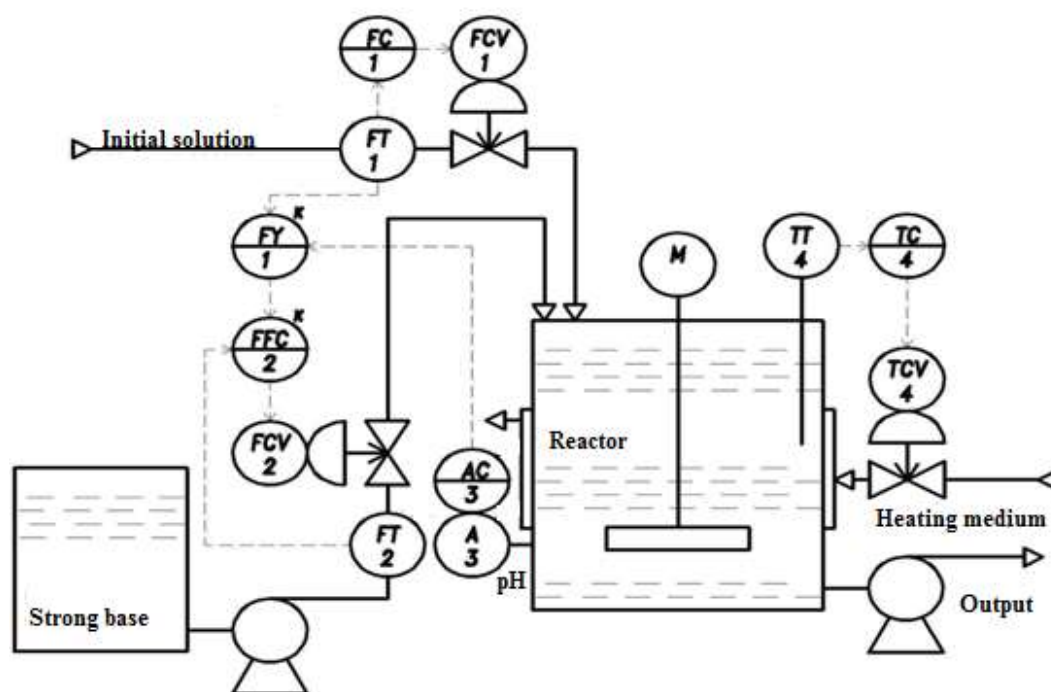


Fig. 2. Scheme of automation of the technological object

Thus, the deviation of the current pH value from the set value is compensated by the change in the specific flow rate. In this case, when the pH meter calibration is shifted (which is not a failure and assumes that the control system remains stable), the regulator will maintain a distorted pH value. However, as shown in [1] from the graph Fig. 1 it follows that the sensitivity of such a method of pH control is quite high in the ranges  $\text{pH}=4\ldots6$  or  $\text{pH}=10\ldots11$ , and in the area  $\text{pH}=6\ldots10$  the method is not effective.

The following assumptions are introduced:

- 1) a single reaction takes place in the system;
- 2) the reaction rate is constant when the concentration of the initial solution is changed in a limited small range;
- 3) the degree of dissociation of the final solution does not change when the concentration of the initial solution changes;
- 4) in the regulated range, the linear relationship between the pH value and the output signal of the pH meter is maintained.

We will continue to assume that the temperature in the reactor is regulated, which allows to exclude the change in the degree of dissociation due to the influence of temperature [4]. Then, when changing the concentration of weak acid  $C^0$  in the initial solution (for example, its increase of real 10% -  $C^{+10}$ ) to maintain the constancy of the pH, it is required that the amount of strong base is also proportionally changed.

Since the flow rate of the initial solution with an increase in the concentration of weak acid does not change, the specific flow rate will increase by 10% due to the growth of the flow rate of the strong base. Then to obtain the titration curve when a 10% increase in the concentration of a weak acid it is

sufficient to increase the specific flow rate by 10% across the entire range. As a result of changes in the concentration, the titration curve is shifted along the abscissa axis (Fig. 3).

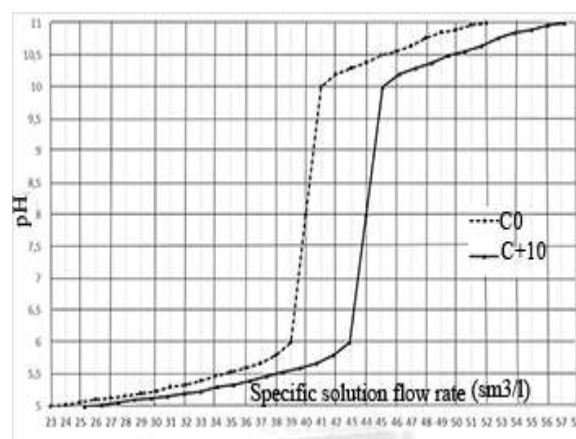


Fig. 3. Titration curve at the concentrations  $C^0$  and  $C^{+10}$  of the initial solution

In the work [1] the basic error of pH-meter was set at the value of  $\Delta\text{pH}=\pm 0,05$ , and the permissible error of pH determination was set at the value of  $\Delta\text{pH}=\pm 0,1$ . It has been assumed above that the additional pH measurement error occurs only due to the deviation from  $C^0$ . Therefore, if the  $C^x$  value is known, then when calculating the permissible deviation of the specific flow rate, the permissible error of the pH should be taken at the level of the basic error of the pH meter.

Fig. 4 for the pH = [5...6] range shows together the graphs of the nominal and boundary values of the specific flow rate at the nominal concentration of  $C^0$  and  $C^{+10}$  ( $\Delta pH = \pm 0,1$ ).

From Fig. 4 it is seen how much has shifted the area of allowable flow rate at pH=5,5. However, at pH=5,3 area of allowable values of the specific flow rate at  $C^{+10}$  partially enters the area of allowable values of the specific flow rate at  $C^0$ . At pH=5, the permissible specific flow rate at  $C^{+10}$  is almost completely within the permitted zone. When the pH < 5, the increasing of the concentration by 10% will not lead to alarm about the displacement of a pH meter calibration. A similar situation will be observed at the concentration of the initial solution  $C^{-10}$ .

Thus, at pH > 5.5 without information on the concentration value, the signal of the pH meter calibration displacement will not correspond to the real pH meter state. At the same time, at pH < 5, the effect of 10% change in concentration will not affect the accuracy of the pH assessment.

The algorithm of the system operation in this case is to compare the real value of the specific flow rate with its permissible values at the measured pH. This comparison is convenient to carry out on the regression model constructed according to data of Fig. 4 and linking specific flow rate with pH values. For example, for the nominal concentration of the initial solution  $C_0$ , a model in the form of 4-degree polynomials ( $R^2=0.9999$ ) can be obtained.

$$F_{\max} = 0,9 \cdot 10^{-4} x^4 - 0,43 \cdot 10^{-2} x^3 + 0,036 x^2 - 0,432 x + 39,68,$$

$$F_{\min} = -0,2 \cdot 10^{-3} x^4 + 0,70 \cdot 10^{-2} x^3 - 0,107 x^2 + 0,048 x + 37,69,$$

where for convenience of calculations the formal variable  $x=20(5.9-\text{pH})+1$  is introduced.

If the actual specific flow rate does not fall within the  $[F_{\min}, F_{\max}]$  interval, the system issues a warning about the pH and specific flow rate mismatch.

The cause of the discrepancy may be a state of pH-meter, and the change in the concentration of the reagent. To specify the cause, it is necessary to carry out an unscheduled laboratory study and adjust the diagnostic model to the shift of the titration curve. Further, to take into account in the diagnostic model the results of the laboratory study, it is sufficient to multiply the boundary model equations by the coefficient corresponding to the measured deviation of the reagent concentration. This will allow to shift the acceptable range of the specific flow rate for continued pH-meter state checks.

## REFERENCES

- [1] Dikhno D.I., Rusinov L.A. Assessment of the pH-meter condition by comparing hydrogen index and flow ratio of reagents. Trudy rudy mezhdunarodnoy nauchnoy konferentsii "Matematicheskiye metody v tekhnike i tekhnologiyakh" [Proc. of the Int. Sci. Conf. "Mathematical methods in engineering and technology"]. Saint Petersburg. 2017, vol.12, pp. 51-56 (in Russian).
- [2] Hints and Tips to Improve Accuracy. In DO and pH Measurement. METTLER TOLEDO Process Analytics (2015). Available at: <http://www.alliancets.com/images/alliancets/PDF/Resources/Mettler-Accuracy-Guide-DO-pH-Measurement-Feb15-ATS.pdf> (accessed 06.01.2018).
- [3] Harriott P. Process Control. New-York. Publ. McGraw-Hill. 1964, 374 p.
- [4] A Guide to pH Measurement. Theory and Practice of pH Applications. Mettler-Toledo AG (2013). Available at: [https://www.mt.com/dam/MTPRO/PDF/GUIDE/pH\\_Theory\\_Guide\\_en\\_30078149\\_Jul13.pdf](https://www.mt.com/dam/MTPRO/PDF/GUIDE/pH_Theory_Guide_en_30078149_Jul13.pdf) (accessed 18.11.2017).

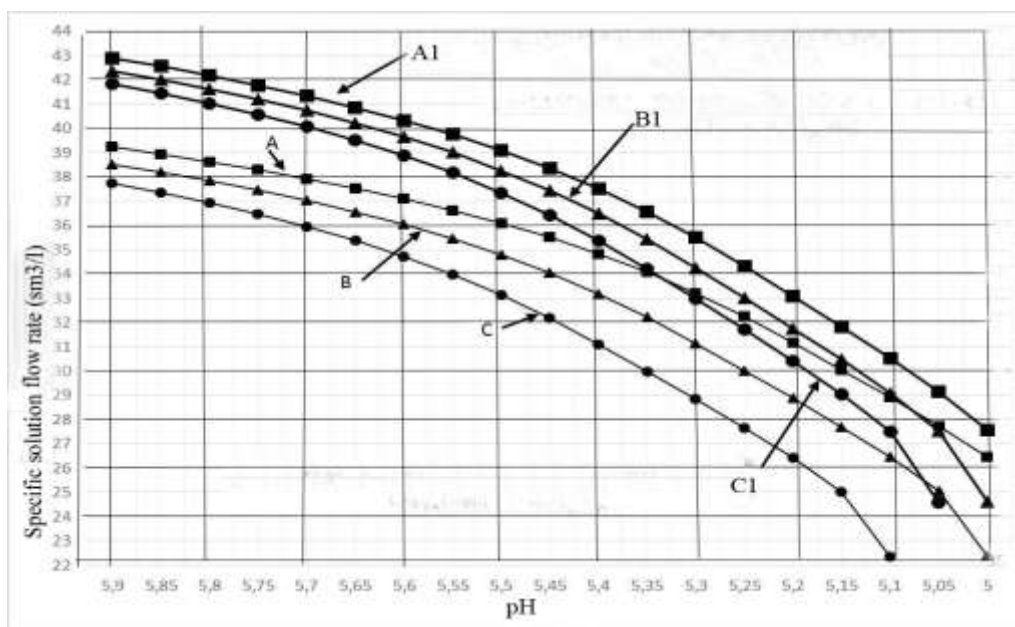


Fig. 4. Graphs of the nominal (B, B1) and boundary (A, A1; C, C1) values of the specific flow rate at the concentrations of  $C_0$  and  $C_{+10}$  respectively