Potentiometric Titration Analysis of Triethylamine and Xylidine Based on Smooth Derivation of Savitzky-Golay

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Abstract. The titration curve is not obvious during the potentiometric titration analysis of the sample containing xylidine, and there is interference noise. The Savitzky-Golay smoothing method is used to eliminate the local noise effect in the titration curve, and the first-order derivation curve is obtained. The method performs polynomial fitting and derivation on each data point in the titration curve by aliquoting the moving window, and obtains the most effective information while eliminating noise. According to the standard sample measurement result error optimization window width and polynomial fitting times, the titration curve is smoothed by five points to obtain the ideal measurement result. The analysis of the actual sample shows that the smooth derivation method can more accurately detect the titration end point of the titration curve, and is simpler, faster and more reliable than the mapping method.

1. Introduction
Potentiometric titration is widely used in the analysis of weak acid and weak base content. It is by measuring the pH value or the potential value of the titration indicating the end point of the titration. Compared with the indicator method, it has the advantages of high accuracy and fast measurement speed. It has significant advantages in the analysis of colored samples, turbid samples and non-aqueous solutions [1-3]. Triethylamine and xylylamine are organic weak bases and the mixture of the two is usually light yellow oil in the air. The content of the components in the mixture is determined by potentiometric titration, which can avoid liquid color interference and low degree of weak base dissociation. The effect of the endpoint determination of the titration makes the detection more accurate and sensitive. Since the two components are similar in basicity, the content of the components in the mixed solution is determined by a back-potentiometric titration method, that is, the sample is first reacted with an excess of hydrochloric acid, and in the acidic aqueous solution of the produced amine salt, the sodium hydroxide standard solution is used. In Potentiometric titration, the titration curve shows two jumps, and the component content is obtained according to the determined titration end point. In potentiometric titration analysis, the determination of the titration end point is crucial. For signal analysis techniques for weak acid, weak base and low content, the titration curve can be effectively determined, and the
accuracy of endpoint detection can be improved. Mrs Shengzhu Si and Mis Liping Wang proposed a method for determining the end point of potentiometric titration by wavelet transform, and successfully applied to the determination of very weak acid content such as phosphoric acid, acetic acid and oxalic acid[4]. Mrs Zhiming Gao et al. studied the experiment of determining the acidic substances in alkyl phosphate and deep well water samples by potentiometric titration, and proposed a method for determining the end point of titration by using BP network combined with one derivative[5]. Ren K. et al. used the rational spline function for the end point determination of potentiometric titration, and applied it to the complex titration with no significant titration, which improved the measurement accuracy[6]. According to the back titration process of the mixed solution, the titration curve corresponding to the second stoichiometric point changes gently, and the local noise interference is characteristic. The Savitzky-Golay smoothing method is used to filter out the titration curve noise, and the titration end point is obtained. The method uses the polynomial to perform the least squares fitting on the data in the moving window, and then derives the effective signal in the local range by weighting the average derivation to emphasize the central role of the center point.

2. Method Principle

The background noise in the potentiometric titration curve is essentially zero random white noise. The original data of the titration curve is divided into a plurality of adjacent or progressive overlapping equal width windows, and the window size is the filtering bandwidth. After the data convolution smoothing is performed by the high-order polynomial in the window, the first derivative of the window center point is obtained. As the window moves, the first derivative of the filtered signal is obtained, and the maximum point is the titration jump point. The method for deriving the data points of the titration curve is as follows:

Let the titration curve have N sampling points. When the width of the window is n, there are 2m+1 sampling points in the window, that is, n=2m+1. In the process of filtering

$$x_i = i \quad (i = -m, -m + 1, -m + 2, \ldots, 0, \ldots, m - 1, m)$$

(1)

Suppose the data points in the window can be fitted with a k-1 degree polynomial.

$$y_j = a_0 + a_1 j + a_2 j^2 + \cdots + a_{k-1} j^{k-1} = \sum_{j=0}^{k-1} a_j \cdot j^i$$

(2)

The above n equations form a k-ary linear equation system. When n=k, the linear algebra method can be used to solve the fitting parameters, $a_j (j = 0, 1, 2, \cdots, k - 1)$ and when n>k, the least squares method is used to solve the problem.

$$\begin{pmatrix}
    y_{-m} \\
    y_{-m+1} \\
    \vdots \\
    y_{m}
\end{pmatrix} =
\begin{pmatrix}
    1 & -m & \cdots & (-m)^{k-1} \\
    1 & -(m+1) & \cdots & (-m)^{k-1} \\
    \vdots & \vdots & \vdots & \vdots \\
    1 & m & \cdots & m^{k-1}
\end{pmatrix}
\begin{pmatrix}
    a_0 \\
    a_1 \\
    \vdots \\
    a_{k-1}
\end{pmatrix} +
\begin{pmatrix}
    e_{-m} \\
    e_{-m+1} \\
    \vdots \\
    e_{m}
\end{pmatrix}$$

(3)

Expressed as a matrix

$$Y_{(2m+1)x1} = X_{(2m+1)xK} \cdot A_{Kx1} + E_{(2m+1)x1}$$

(4)

Least squares solution

$$\hat{A} = (X^T \cdot X)^{-1} \cdot X^T \cdot Y$$

(5)

Use the 2m+1 data of the filter window to find the first derivative of the window center point $(i = 0)$. 

$$\left( \frac{\partial y_i}{\partial t} \right) = a_1$$

(6)

When the m and k values are given, the position of the window is sequentially shifted, and the first derivative of the original data of the titration curve from the $m+1$ point to the $N-m$ point can be obtained.
m is related to the width of the moving window. The window width is too small, the noise removal effect is not good, and the window width is too large, which will make the smooth data distorted. Therefore, when using this method, it is necessary to optimize the width of the moving window and select the appropriate polynomial fitting times to achieve the best denoising effect and accurately extract the effective information.

3. Experimental Part

3.1. Instruments and Reagents
The main instruments used in this experiment were Mettler-Toledo's T50 automatic potentiometric titrator and DG113−SC composite glass electrode. The reagents used included a 0.5 mol/L hydrochloric acid standard solution and a 0.5 mol/L sodium hydroxide standard solution. Ten samples of industrial waste liquid containing triethylamine and xylylamine were taken as experimental samples. A standard sample with 11 xyleneamine concentrations evenly distributed between 30% and 50% was prepared.

3.2. Experimental Methods
Take 50 mL of distilled water into the measuring cylinder, pour into the titration cup, add about 45 mL of hydrochloric acid standard solution with a burette and record the volume, and start mechanical stirring. A weighed 2mL sample was pipetted and slowly injected into the acidic solution. The titration was carried out with a sodium hydroxide standard solution, the volume of a single titration was set to 0.1 mL, and the pH value was recorded until the end of the neutralization reaction, and a titration curve of two jumps was obtained. Among them, the first stoichiometric point is obtained by the second derivative algorithm, and the second sudden titration curve is processed by the Savitzky-Golay smoothing derivation method to obtain the titration volume of the stoichiometric point. The triethylamine content was calculated by adding the amount of hydrochloric acid and the amount of sodium hydroxide corresponding to the second stoichiometric point, and the xylidine content was calculated using the amount of sodium hydroxide consumed between the first and second stoichiometric points.

4. Results and Discussion

4.1. Titration Curve Analysis
Ten samples were measured according to the above experimental methods, and a representative pH-V curve was obtained as shown in Figure 1.

It can be seen from Fig. 1 that the titration curve contains 32 data points, the jump is not obvious, and the local range has fluctuations caused by random noise, which interferes with the determination of the curve jump point. In this paper, the Savitzky-Golay smoothing derivation method is used to
smooth out the data points except the edge points by moving the window, and the local noise interference is eliminated. The obtained values of the points are in line with the curve trend.

4.2. Window Width and Polynomial Number Selection
For the titration curve of 11 standard samples, the polynomial fitting times are optimized between 2 and 3. The window width is from 3 to 13 points, and the interval is incremented by 2. According to the relative error between the measured value of the xylidine content and the true value of all samples. The mean value selects the optimal window width and the result is shown in Figure 2.

![Figure 2](image)

Figure 2. The choose of Savitzky-Golay’s window level and degree of polynomial window
As can be seen from Fig. 2, the error in the measured value of the xylidine content in the window width increase first decreases and then increases. When the number of polynomial fittings is 2 and the window width is 5, the measurement error reaches a minimum of 0.56%, which is the best condition for smooth derivation.

4.3. Determination of actual samples
Since the 10 samples taken do not contain other impurities that interfere with the titration, the first-order smoothing of the titration curve of the unknown concentration sample is performed in the same manner as the standard sample titration curve. The derivative curve obtained by smooth derivation in Fig. 1 is shown in Figure 3.

![Figure 3](image)

Figure 3. The derivative curve obtained by Savitzky-Golay smoothing method
As can be seen from the above figure, the second stoichiometric point of the sample titration is the maximum point of the smooth derivation curve, and the titration volume corresponding to the sodium hydroxide standard solution is 27.80 mL. The second stoichiometric point in the titration process was determined by the above method for all 10 samples to be tested. The content of xylidine and triethylamine in the sample was calculated by adding the amount of hydrochloric acid and the amount of the two stoichiometric titrants as shown in Table 1.
Table 1. Analysis of the content of xylidine and triethylamine in the sample

| Sample No. | V$_1$/ml | V$_2$/ml | X$_1$/% | X$_2$/% |
|------------|----------|----------|---------|---------|
| 1          | 6.40     | 22.41    | 39.6    | 60.4    |
| 2          | 8.68     | 24.44    | 41.1    | 58.9    |
| 3          | 7.04     | 22.57    | 40.2    | 59.8    |
| 4          | 10.14    | 26.34    | 41.7    | 58.3    |
| 5          | 11.32    | 25.43    | 43.7    | 56.3    |
| 6          | 14.04    | 29.88    | 45.1    | 54.9    |
| 7          | 10.82    | 27.53    | 46.5    | 53.5    |
| 8          | 16.74    | 32.47    | 47.3    | 52.7    |
| 9          | 18.30    | 30.54    | 49.5    | 50.5    |
| 10         | 20.00    | 36.54    | 49.9    | 50.1    |

The xylidine content of the test sample is within the range of the concentration of xylamine in the standard sample, which meets the requirements of the experimental measurement conditions. In order to verify the reliability of the experimental measurement method, the same sample was measured in parallel five times, and the measurement results were compared with the mapping method [7], as shown in Table 2.

Table 2. Repeatability of measurement results

| Measuring method | Measurement value,X% | Average value, $\bar{X}$% | Standard deviation,S |
|------------------|-----------------------|---------------------------|----------------------|
| Smooth Derivation Method | 38.8 | 39.4 | 39.6 | 39.7 | 40.2 |
| Drawing method   | 39.6 | 39.9 | 40.7 | 41.2 | 41.5 |

It can be seen from Table 2 that the standard deviation $S_{min}$ of the measured value of the smoothing derivation method is smaller than the standard deviation $S_{max}$ of the measured value of the mapping method, indicating that the smoothing derivation method analyzes the titration curve, and the experimental result with higher precision can be obtained. The F test was performed on the measured values of the two methods at 95% confidence[8]. Wherein, $F=S_{max}^2/S_{min}^2=9.51$, and there is a maximum value of 6.39 which is significantly different from the five measurements. Therefore, the smooth derivation method significantly improves the precision of the experimental results and has higher reliability than the mapping method.

5. Conclusion

From the above analysis, it can be seen that the smooth derivation method is applicable to the detection of the sudden jump point of the sample potential titration curve without obvious jump and local noise. The method can eliminate the interference noise of the titration curve and accurately extract the effective information by moving the window to the local range. It has the characteristics of faster and more reliable than the mapping method, and is practical in the potentiometric titration analysis of weak acid and weak base.

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