Study on analysis of acid number of transformer oil by temperature titration

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Abstract. Important test methods for acid number of oil products were introduced, and their characters, difference and selection Principle were described. And the temperature titration method was used to determine the acid number of transformer oil. Meanwhile, several major factors that may affect the outcome were discussed.

1. Introduction

Acid value is an important indicator of petroleum and its products. Size is a measure of the amount of acid Content. Understanding the content and distribution of acidic substances is conducive to better Control product quality. [1].

At present, there are many standard methods for acid value determination, including new oil and running oil; there are national standards, ministerial standards and industry standards. These standards are roughly divided into 2 categories: Indicator method and potentiometric titration method [2]. Over the years, these two methods have played a considerable role in the monitoring and maintenance of power oil, but there are also obvious shortcomings: indicator method needs heating and reflux, which is time-consuming and laborious. In addition, carbon dioxide is easily intruded into the solution during titration, which affects the results of determination. The color mutation at the end of titration is also prone to errors due to subjective judgment; the preparation time of potentiometric titration method is too long, and the operation is too complex, the electrode is easy to passivate. Besides, more time-consuming and laborious, and toxic solvents need to be used in the operation process, so the safety is difficult to guarantee. It is for these reasons that, although the importance of acid value determination is known in many laboratories of grass-roots units, it has been delayed and can not be carried out normally. Therefore, it is necessary to develop a temperature titration acidity determination method with fast speed, easy operation and accurate results.

2. Structure and Characteristics of Titration Tank

The working principle of the titration tank is shown in Fig. 1. A certain quantity of oil sample to be measured was poured into the titration tank, and then reagent 1 (extraction solvent) and reagent 2
(temperature indicator) with the given volume of solvent were injected into the titration tank through quantitative pump 1 and pump 2, respectively. The oil sample to be measured, reagent 1 and reagent 2 in the titration tank were fully mixed by magnetic stirrer. Reagent 3 (titration reagent) was slowly injected into the titration tank through the quantitative pump 3 at a certain speed. Because of the addition of reagent 3, the acidic components, reagent 1 and reagent 2 in the oil sample began to react chemically, accompanied by enthalpy change of the reaction system showing endothermic or exothermic phenomena. At this time, the temperature sensor continuously measured the temperature of the mixed liquid in the reaction tank, and the temperature change was displayed on the display by the processing circuit in real time, thus the curve of temperature change with the volume of reagent 3 was drawn. By analyzing the curve of the treatment circuit, the inflection point of endothermic and exothermic reaction was determined, which is the consumption of reagent 3. The acid value of the oil sample to be measured was calculated by the consumption of reagent 3. The acid value results were output to the display and printer, and the test was completed.

![Fig 1. Schematic diagram of working principle of titration tank](image)

The structure of the titration tank can met the requirement of automatic operation. The acid value of oil sample can be obtained quickly by automatic sampling and titration by quantitative pump, continuous stirring of magnetic stirrer, continuous measurement of temperature sensor and intelligent analysis and calculation of microprocessor.

3. Results and Discussion

3.1. Preparation of standard acid

Benzoic acid (chemical formula: PhCOOH) is a weak acid to verify the accuracy of temperature titration. Its acidity coefficient pKa = 4.20 is commonly used as standard acid in the determination of acid value of oil products. In general, a certain concentration of benzoic acid solution was prepared by dissolving a certain amount of benzoic acid in isooctane. The standard curve was drawn by the mass of the standard acid and the consumption volume of the titration reagent, and the accuracy and reliability of the test results were judged. Because the acid value of transformer oil was generally small, the standard acid value of the prepared transformer oil should not be different from the standard requirement. The standard acid value of 0.02 mg KOH/g was prepared to establish the standard curve. The formula for calculating the standard acid value is as follows:
X= m1/ m3                                    (2)
m1= 56.1×m2/122.1                                (3)
m2= C1×122.1×V1                                (4)
V1= /ρIsooctane= m3/0.6919                            (5)

Where: X——the acid value of the prepared standard acid, mgKOH/g
C1——Concentration of benzoic acid in standard acid, mol/L
m1——Mass of KOH consumed in titration process, mg
m2——Mass of weighted benzoic acid in standard acid sample, mg
m3——Mass of weighted standard acid samples, g
V1——Volume of standard acid samples (calculated by isoctane, neglecting trace benzoic acid), mL

The formula for calculating the theoretical acid value of benzoic acid standard acid was obtained by formula (2) ~formula (5) substitution method.

X=56.1×m/122.1×0.6919×V=0.6641×m/V                      (6)

Therefore, 0.0151g benzoic acid was dissolved in 500 mL isoctane, and the standard acid solution with theoretical acid value of 0.02 mg KOH/g can be prepared according to formula (6).

3.2. Drawing Standard Curve

The standard acid solutions of 7.0g, 8.5g, 10.0g, 11.5G and 13.0g were weighed accurately respectively. According to the determination of the previous test conditions, 25 mL acetone and 4 mL trichloromethane were added automatically by the determinator to mix evenly, and 0.10mol/L potassium hydroxide ethanol standard solution calibrated by potassium phthalate was added at a constant rate of 1.0mL/min. The end point of titration was judged by the temperature abrupt change and the volume of titration reagent consumed was calculated. Each mass point of the standard acid solution was determined three times. The average volume of the titration reagent consumed was calculated as shown in Table 1.

| No. | Mass of standard acid(g) | Titration volume(mL) | Measured standard acid value(mgKOH/g) |
|-----|-------------------------|----------------------|---------------------------------------|
| 1   | 7                       | 0.067                | 0.0206                                |
| 2   | 8.5                     | 0.073                | 0.0209                                |
| 3   | 10                      | 0.077                | 0.0200                                |
| 4   | 11.5                    | 0.084                | 0.0208                                |
| 5   | 13                      | 0.089                | 0.0206                                |

The mass of standard acid (g) is plotted by the consumption volume of titration reagent (mL), and the standard curve is shown in Fig. 3. The linear regression equation Y=0.0037X+0.0413 was fitted by excel software, and 0.0413 (mL) was the blank value under this test condition. As showed in Fig. 2 that the square of correlation coefficient is 0.9951.
Fig 2. Standard curve of standard acid

According to the formula of acid value calculation (formula 7) and the blank value in regression equation, the actual standard acid value was calculated. The results are shown in Table 1. From Table 1, it can be seen that the average value of the standard acid value measured in practice is 0.0206 mg KOH/g, which is basically consistent with the theoretical acid value of 0.02 mg KOH/g, and the repeatability of the results is fine, and RSD is 1.70%. This indicates that the standard curve has been successfully established, which provides a reliable basis for further verifying the relevant test of the oil samples to be measured.

\[
X = \frac{(V - V_0) \times 56.1 \times C}{G}
\]  

(7)

Where: 
- \(X\)——Acid value of oil sample, mgKOH/g
- \(V\)——Volume of KOH ethanol solution consumed during titration, mL
- \(V_0\)——The blank value under this test condition, mL
- \(C\)——Concentration of KOH ethanol standard solution (calibrated by potassium hydrogen phthalate), mol/L
- \(G\)——Mass of oil sample, g).

3.3. Test of accuracy

The determination of acid value of transformer oil was mainly based on the methods specified in NB/SH/T 0836 and GB 264-83 standards. Because the color of transformer oil was generally lighter, it was not easy to cover up the color determination of titration end point, and the indicator titration method was more convenient, the GB 264-83 standard method and the temperature titration method were used to compare the test, in order to verify the accuracy of the temperature titration method to determine the acid value of transformer oil.

According to GB 264-83, Alkali Blue 6B was used as indicator to change the color from blue to light red at the end of titration. In the experiment, KOH standard solution was calibrated by potassium hydrogen phthalate with a concentration of 0.0205 mol/L, and the mass of oil samples to be measured ranged from 8 to 10g. The KOH ethanol standard solution for temperature titration was also calibrated with potassium hydrogen phthalate at a concentration of 0.10 mol/L. The blank value was 0.0413 mL, and the mass of the oil sample to be measured was between 8 and 11g. The oil samples to be tested were transformer oil entrusted to our institution by Shandong provincial power supply companies and power plants, including new oil, pre-commissioning oil and running oil. The test results are shown in Table 2.
### Table 2. Contrastive test of Alkali Blue 6B method and temperature titration method for determining acid value of transformer Oil

| No. | Device names                                    | Sample description | Alkali Blue 6B method | Temperature Titration |
|-----|-------------------------------------------------|--------------------|-----------------------|-----------------------|
|     |                                                 |                    | Oil sample mass (g)   | KOH Ethanol volume (mL) | Acid value (mgKOH/g) | Oil sample mass (g) | KOH Ethanol volume (mL) | Acid value (mgKOH/g) |
| 1   | Binzhou Power Supply Company #2 New Oil         | New oil            | 9.93                  | 0.02                  | 0.002                | 9.25                | 0.058                  | 0.010                |
| 2   | Taikai Transformer Company New Oil              | New oil            | 9.15                  | 0.03                  | 0.004                | 9.66                | 0.060                  | 0.011                |
| 3   | 500 kV # Main Transformer C Phase of the Yellow River in Shandong Power Transmission and Substation | New oil            | 8.98                  | 0.05                  | 0.007                | 10.23               | 0.065                  | 0.013                |
| 4   | 500 kV #2 Main Transformer Phase A in Shandong Power Transmission and Transformer Oil City | New oil            | 8.76                  | 0.04                  | 0.005                | 8.77                | 0.058                  | 0.011                |
| 5   | 110kV#2 Main Transformer of Shandong Liancheng Electric Power | Before discharge | 9.09                  | 0.04                  | 0.005                | 9.42                | 0.061                  | 0.012                |
| 6   | 220 kV #2 Main Transformer in Feidong of Shandong Transmission and Substation | Before discharge | 9.33                  | 0.05                  | 0.006                | 8.90                | 0.060                  | 0.012                |
| 7   | 220 kV #2 Main Transformer in Island Power Plant | Before discharge | 9.23                  | 0.03                  | 0.004                | 9.71                | 0.060                  | 0.011                |
| No. | Action | Power Plant | Transformer | Running Oil | Penetration | Water | Oil | Wg | Water | Oil | Wg |
|-----|--------|-------------|-------------|-------------|-------------|-------|-----|----|-------|-----|----|
| 8   | Oil penetration welding | 220 kV #2 Main Transformer in Dongying of Shandong Power Transmission and Substation | 9.02 | 0.06 | 0.008 | 10.11 | 0.067 | 0.014 |
| 9   | Running oil | #1 Main Transformer of Dafeng Station of Dongyue Energy in Shandong Province | 9.27 | 0.06 | 0.007 | 10.04 | 0.066 | 0.014 |
| 10  | Running oil | Main Transformer of Shandong Dongyue Energy National Day Station | 9.38 | 0.02 | 0.003 | 9.87 | 0.061 | 0.011 |
| 11  | Running oil | Main Transformer of Huaneng Jining Power Plant | 9.11 | 0.03 | 0.004 | 9.98 | 0.059 | 0.010 |
| 12  | Running oil | #1 Start-up and Standby of Huaneng Jining Power Plant | 8.95 | 0.04 | 0.005 | 10.15 | 0.061 | 0.011 |
| 13  | Running oil | #4 Main Transformer of Huaneng Laiwu Power Plant | 9.19 | 0.08 | 0.010 | 9.66 | 0.067 | 0.015 |
| 14  | Running oil | #4 High Voltage Plant Change of Huaneng Laiwu Power Plant | 9.10 | 0.04 | 0.005 | 9.50 | 0.062 | 0.012 |
| 15  | Running oil | Guoneng Wuqiao Biopower Company | 10.0 | 0.04 | 0.005 | 10.02 | 0.061 | 0.011 |
Origin 7.5 was used to fit the correlation between the acid values measured by the two methods in Table 2 by the least square method. The relationship curve obtained is shown in Figure 4. The regression equation is \( Y=0.00818+0.69186X \), and the correlation coefficient \( R \) is 0.92996. It can be concluded that the two methods are highly correlated. The equation can be used to convert the results of two different acid value determination methods. It also showed that the accuracy of the temperature titration method is basically in line with the expected goal.

4. Conclusion

(1) Based on the investigation of the theory of temperature titration, the principle of measuring acid value of transformer oil by temperature titration and the basic reaction formula of solution system in the process of measuring were put forward.

(2) After a lot of experiments, extraction solvent, temperature indicator and titration reagent were selected, the dosage and preparation method of various reagents were mastered.

(3) The standard acid was selected by the optimized test method, the standard curve was drawn, and the blank value under this method was established.

(4) Through the repeatability test of five oil samples, it was proved that the accuracy of temperature titration method for determining acid value of transformer oil was high.

References

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