Experimental Study on Rapid Determination of Acid Value of Oil by Temperature Titration

Suhong Chen¹, *, Yufeng Chen¹, Zhijun Han², Gao Feng³, Xiangkun Pang¹ and Lei Zhang¹

¹State Grid Shandong Electric Power Research Institute, Jinan 250003, China
²State Grid Shandong Electric Power Company, Jinan 250001, China
³State Grid Licheng Power Supply Company, Jinan 250100, China

*Corresponding author e-mail: qingxinsmile@163.com

Abstract. In this paper, the method for detecting the acid value in transformer oil was studied, and the temperature titration method was used to determine the acid value of transformer oil. Meanwhile, several major factors that may affect the outcome were discussed.

1. Introduction

Oil-filled electrical equipment such as transformers is an important core equipment in substations of power system, and its reliable and safe operation is crucial. Once a fault occurs, it directly affects the safe and stable operation of the power grid. The transformer oil used in the power system is a kind of mineral insulating oil whose main chemical compositions are alkanes, naphthenes and aromatic hydrocarbons. Under the action of oxygen, heat and electric field, transformer oil in electrical equipment will gradually aging in operation, which will increase the acidity of oil. Acidic substances not only corrode equipment, but also improve the electrical conductivity of oil products and reduce the insulation performance of oil, which ultimately shorten the life of oil-filled electrical equipment and cause huge losses. In order to ensure the normal operation of equipment and prolong its service life, it is necessary to strictly monitor and maintain transformer oil. The indicator that reflects the content of acidic substances in oil - acid value is the main monitoring parameter. In China's standards and international standards, acid value is listed as mandatory parameter [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. Principle of acid value measurement by temperature titration
A certain mass of oil sample to be measured was added to the titration vessel with thermal insulation function, and the stirring device was opened to make the titration vessel closed. A certain amount of extraction solvent and temperature indicator were added in turn to make the solvent and the oil sample to be measured fully mixed in a certain period of time. The temperature sensor then transmitted the current temperature signal to the computer record and took the temperature as the starting temperature of titration. After that, the titration reagent (usually KOH ethanol solution) was added to the titration container at a constant speed by a high precision injection quantitative pump. With the increase of titration reagents, several mixed liquids in the titration vessel reacted chemically and produced thermal effect, which resulted in the temperature change of several mixed liquids in the vessel. In this process, the computer used the temperature sensor to sample the temperature value at a high speed, and drawn the temperature-titration volume curve of the titration system. The temperature titration curve was analyzed to determine the time point when the sudden leap occurred. The consumption of the titration reagent was calculated according to the titration speed and the sudden leap time point of the titration reagent, and the acid value of the oil sample to be measured was calculated by the following formula [3]:

\[ X = 56.1 \times N \times V / G \]  

Where,  
- \( X \) —— acid value of oil sample, mgKOH/g
- \( N \) —— Concentration of KOH ethanol solution, mol/L
- \( V \) —— Volume of KOH ethanol solution consumed during titration, mL
- \( G \) —— Mass of oil sample, g

Fig. 1 is a thermogram of acid-base neutralization titration by temperature titration. Fig. 1 (a) and Fig. 1 (b) show the temperature titration curve of exothermic reaction in the titration process system. With the titration proceeding, the temperature of the system increases gradually. When the titration end point was reached, the temperature of the system decreases sharply or no longer increases. The inflection point of temperature change (also known as sudden jump point or sudden change point) is the end point of titration. The abscissa corresponding to this point is the volume of the titration reagent consumed. Fig. 1 (c) and Fig. 1 (d) show the temperature titration curve of endothermic reaction in the titration process system. With the titration proceeding, the temperature of the system decreases gradually. When the titration end point was reached, the temperature of the system increases sharply or no longer decreases. If a suitable reaction system can be found and the temperature titration curves of Fig. 1 (a) and Fig. 1 (c) can be shown by the method of temperature titration, then it was the most ideal state, which will make the temperature jump more obvious and the result can be more accurate.
3. Results and Discussion

Once the reagent was determined by temperature titration, the trend of enthalpy change was determined. At this time, finding the appropriate reaction conditions can make the temperature titration curve more sensitive and the sudden jump point clearer, so as to make the determination results more accurate. The acid value determination of transformer oil mainly considers the setting of test conditions from five aspects: the amount of extraction solvent and temperature indicator, the mass of oil sample to be measured, the mixing time of reaction reagent, the concentration of titration reagent and the titration speed.

The volumes of extraction solvent and temperature indicator were adjusted by using the developed temperature titration acidity analyzer. A large number of experiments showed that the enthalpy of the reaction system changed obviously when 20 mL acetone and 4 mL trichloromethane were added into the titration tank, and the temperature titration curve was ideal. In this way, the volume of acetone and trichloromethane was determined.

The mass of oil samples to be measured was generally between 5g and 15g when the acid value of oil used in electric power was determined by different methods. In the experiment of measuring acid value of transformer oil by temperature titration, we found that under certain conditions, the mass of oil sample was less than 7 g or more than 13 g, which will have a certain impact on the accuracy and repeatability of the results. The curvature of titration curve is small, which makes the judgment of the result not too obvious. Therefore, we determined the weighing range of the oil samples to be measured was 7g~13g.

The mixing time of acetone and trichloromethane also need to be determined. If mixing time was too long, the rising of temperature effect caused by mixing of different specific heat capacity reagents will gradually disappear, and then exothermic reaction will occur in acid-base neutralization titration, which
made the system temperature rise. If the mixing time was too short, the titration of the tested oil sample and reagent will begin before they can be fully mixed, the temperature of the system may fluctuate, or even have no downward trend, leading to the difficult identification of the sudden jump point. Through experiments, the mixing time of acetone and oil samples to be measured was 40s, and then 30s with trichloromethane.

The sensitivity of titration end point was affected by many factors, such as reaction equilibrium constant, concentration of reaction components, reaction speed, reaction heat and so on. It can be seen that once the concentration and speed of the titration reagent were properly selected, the temperature jump will become more sensitive and clear. Generally speaking, the higher the concentration of titration reagent, the faster the titration speed and the more sensitive the titration end point. However, from the point of view of the accuracy of analysis, the use of large volume titration can obtain certain benefits, but the benefits of increasing the consumption of titration reagents will be offset by the decrease in the repeatability of the results. Because the acid value of transformer oil was small (the new oil standard was not greater than 0.01 mg KOH/g, the running oil standard was not greater than 0.1 mg KOH/g), the concentration of titration reagent should not be too large, otherwise, the titration volume will be smaller, the test error will be increased and the accuracy of determination will be affected, too small concentration and increasing the titration volume will reduce the repeatability. The same principle applied to titration speed. Therefore, we chose the titration reagent potassium hydroxide ethanol solution concentration was 0.1 mol/L, titration speed was 1.0 mL/min through a large number of experiments.

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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