Aging Analysis of Transformer Mineral Insulating Oil Based on Chromatographic Furfural Content Determination

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Abstract. The concentration of furfural in transformer oil is an important indicator of the degree of aging of insulating paper. By measuring the content of furfural in the transformer oil, it is possible to understand the degree of aging of the insulating paper and estimate the residual life of the transformer. In this paper, we introduce a principle and method for the determination of trace furfural in transformer oil by high performance liquid chromatography. The measured data show that the method is small, simple, and sensitive, which is of great significance for diagnosing the aging of transformer insulation paper.

1. Introduction
For many years, the power system mainly used gas chromatography to analyze the dissolved gas content in transformer oil to determine whether there is a latent fault in the transformer. However, there is no way to detect the degree of overheating of paper insulation in transformers. This is because the characteristic gases CO and CO2 of insulating paper are also characteristic gases of insulating oil, and have much to do with other factors such as the sealing property of the equipment [1]. Due to the diversity and complexity of the internal faults of the transformer equipment, only the gas chromatographic analysis of the dissolved oil of the transformer oil to judge the condition of the equipment cannot meet the needs of power development, and the characteristic products of the aging of the insulating paper are analyzed by liquid chromatography. It is especially important to judge the aging degree and operating condition of the transformer to supplement the shortage of gas chromatography.

At present, the insulating paper materials of large domestic power transformers mainly use wood pulp as raw material, and its main chemical component is cellulose [2]. The cellulose macromolecule is a chain multi-molecular polymer composed of about 1200 glucose ring monomers. In the long-term operation of the transformer, due to the influence of temperature, moisture, organic acids, impurities, etc., the transformer insulating paper material is finally oxidized and cracked into small molecule degradation products, among which the furfural compound is the main characteristic product. These small molecules of liquid compounds are gradually dissolved in the transformer insulating oil and are subjected to oil circulation to achieve a uniform concentration.
Since the furfural compound is the main product of the aging of the paper insulating material, its content is closely related to the aging degree of the paper insulating material. Therefore, by periodically sampling and testing the transformer oil, the purpose of monitoring the aging of the paper insulating material can be achieved.

The results show that the content of furfural in oil can be used as an indicator of transformer insulation aging, especially insulation paper aging. The aging rate of insulating paper is constantly changing during the operation of the transformer, especially due to the high temperature caused by local overheating and overload. The high furfural content indicates that the mechanical strength of the insulating paper has been reduced to a very low level. At this time, the risk of transformer failure is quite large, and the relatively low furfural content does not mean that the transformer must have a large insulation margin because it occurs in Local failures in the weakened insulation paper can also pose considerable risks [3]. Significant changes in furfural content in just a few months indicate that there is a high probability of a hidden danger inside the transformer and causing a fault, so it is necessary to periodically detect the furfural content in the transformer oil.

2. Test method and selection of test parameters
Furfural is a non-ionic polar compound, and transformer oil is mainly composed of non-polar or weakly polar compounds such as alkenes and small amounts of aromatic hydrocarbons [4]. Therefore, the furfural in the transformer oil can be extracted by using a relatively strong methanol reagent to reduce the interference of a large number of non-polar or weakly polar components in the oil, and then the furfural in the extract is separated by reversed-phase chromatography. The electron interactions on the three zero bonds in the furfural molecule form a conjugated large zero bond and have a strong absorption of ultraviolet light of a certain wavelength, so that the chromatographic separation of furfural can be performed with a high sensitivity ultraviolet detector. The data was processed and calculated by a chromatography workstation to determine the furfural content of the oil.

2.1. Mobile Phase, Flow Rate and Column Temperature Selection
The use of methanol and water as a mobile phase allows the furfural in the extract to separate from the impurity components in the column. Tests by different ratios show that: when using 55% - 85% methanol water. When the solution is eluted, the furfural peak and the adjacent interference peaks can not only be completely separated, but also the peak height can meet the sensitivity requirements of the test.

In order to test the optimum ratio of the applicable instruments, experiments were carried out with aqueous solutions of 55%, 60%, 75%, and 85% of the mobile phase. The sensitivity and resolution of furfural and solvent peaks are constantly changing under different flow conditions. The measured data is shown in Tab. 1. From the data in the table, it can be seen that when the flow phase is selected with 60% methanol aqueous solution, the sensitivity are higher.

| Table 1. Furfural sensitivity and resolution. |
|---------------------------------------------|
| parameters | Mobile phase concentration |
| H/cm       | 55% | 60% | 75% | 85% |
| H/cm       | 3.20| 3.71| 3.53| 3.29|
| R          | 1.31| 1.25| 1.15| 0.87|

As can be seen from Tab. 2, when the flow rate is 0.8 ml/min, the peak height is high, the peak area is the largest, the retention time is the longest, and the pressure before the flow pump column is small; the flow rate is 0. When 0.8 ml/ min, the peak height is the highest, the peak area is larger, and the retention time is longer, but the pressure before the flow pump column is higher; when the flow rate is 1.2 ml/min, the peak height and the peak area are the smallest. The question is the shortest, so it is advisable to select a flow rate of 1.0 ml/min.
Table 2. Detection flow selection.

| Flow/mL·min⁻¹ | Remain times/min | Peak height/µAU | Peak area/µAU·s | Pressure/Mpa |
|---------------|------------------|----------------|-----------------|--------------|
| 0.8           | 4.785            | 51896          | 89562           | 13.5         |
| 1.0           | 4.985            | 53258          | 77658           | 15.3         |
| 1.2           | 1.125            | 48564          | 52699           | 18.5         |

Increasing the temperature will make the separation of the column better, but it will also cause the retention time of the detection material to advance. Considering the temperature of the column to 35 °C, the separation effect, retention time and repeatability of the detection can be optimized.

2.2. Detection Wavelength Selection

The Furfural and its derivatives undergo maximum light absorption at wavelengths of 260 to 290nm. Under the same conditions, the wavelength of the UV detector is changed, and the peak height of the spectrum is measured. As shown in Tab. 3, the peak area of furfural is the largest at 275 nm, so the detection wavelength is set at 275nm.

Table 3. Three Scheme comparing.

| Wavelength/nm | 260 | 270 | 275 | 280 | 285 | 290 |
|---------------|-----|-----|-----|-----|-----|-----|
| Peak height   | 22.0| 28.5| 34.7| 58.3| 41.5| 31.0|

2.3. Extraction Time Selection

The detection wavelength was chosen to be 275 nm. The mobile phase methanol was chosen to be 60%. Select different extraction time, when the extraction time reaches 1 minute, the peak area and peak height do not change much, so the extraction time is selected as 1 minute.

3. Mass concentration calculation

3.1. Relation Curve Calculation

In the chromatographic liquid phase method, the content of furfural is linear with the peak height measurement. In order to obtain the function curve of the concentration of furfural and the peak height of the liquid phase, we prepared different concentrations of furfural standard solution, and measured the peak height under the optimal conditions obtained by the test. The test results are shown in Tab. 4.

Table 4. Test results.

| Mass concentration(mg/L) | Peak height(mV) |
|-------------------------|-----------------|
| 1.0                     | 101.5           |
| 2.0                     | 197.3           |
| 4.0                     | 435.6           |
| 6.0                     | 615.3           |
| 8.0                     | 856.7           |

After linear regression fitting by computer, the relationship between concentration and peak height is obtained, as shown in (1). At the same time, the fitted relation curve is shown in Fig. 1.

\[ y = 107.2x - 9.07 \quad R = 0.998 \quad (1) \]
3.2. Extraction Model
The content of furfural in transformer oil is very low. When testing, it is necessary to pre-treat the oil sample to concentrate the furfural. The extraction method is used to concentrate the furfural in the oil, and the organic impurities in the oil are also avoided [5]. The extraction rate is relatively stable in the range of 19 °C to 30 °C. Under the above test conditions, it is reasonable to take 0.66. The value of ρ at 50 °C is not only small, but also highly dispersible, because the boiling point of methanol is low, only 65 °C at 1 atmosphere and the boiling point is lower at high altitude, during the test. A large amount of vaporization of methanol occurred, and therefore, the test data was inaccurate. In the test, for the accuracy of the test, the test is reasonable at room temperature, and it is necessary to prevent vaporization of methanol caused by excessive temperature.

3.3. Extraction Model
In order to evaluate the repeatability of the method, four oil samples in different content ranges were selected and the repeatability test was carried out. The measurement results are shown in Tab. 5.

| Oil No.(mg/L) | Test1 | Test2 | Test3 | Test4 | Test5 |
|--------------|-------|-------|-------|-------|-------|
| 1            | 0.52  | 0.51  | 0.50  | 0.49  | 0.50  |
| 2            | 0.021 | 0.022 | 0.022 | 0.021 | 0.019 |
| 3            | 1.09  | 10.7  | 1.08  | 1.08  | 1.08  |
| 4            | 2.41  | 2.38  | 2.39  | 2.41  | 2.40  |

It can be seen from the above table that the deviation of different measurement results of the same sample is within 3%, and the test method has good repeatability.

In order to evaluate the stability of furfural content in insulating oil, we selected a certain amount of furfural oil sample, measured the content after vacuum degassing and oscillating degassing, and compared with the normal test content to determine the change. The results of multiple comparison tests show that even at a temperature of 50 °C, the oscillating degassing has no effect on the furfural content in the oil. The vacuum degassing has a great influence on the furfural content in the oil, especially the transformer oil treatment. The vacuum degassing is carried out for several tens of hours, and therefore, the loss of furfural content in the oil is not negligible [7]. Therefore, the oil sample is stored under normal room temperature conditions, the furfural is not easily lost, and the furfural content in the oil is stable.

4. Transformer aging analysis
For transformers that are put into operation soon or are not well sealed and have high operating temperatures, it is unscientific to rely solely on the determination of the volume fraction of carbon monoxide and carbon dioxide to determine the degree of paper insulation aging. Furfural is affected not only by the type of paper, but also by temperature. Under normal circumstances, the temperature of the transformer during normal operation will not exceed 100 degrees Celsius, but if there are some faults in
the operation of the transformer, such as corona, partial discharge, spark discharge, etc., or the transformer is overloaded, the temperature inside the transformer will be It will rise, which will increase the amount of furfural that the solid material degrades into [6]. Therefore, it is possible to monitor the aging of the transformer and the fault of the transformer with furfural.

There is a certain relationship between the content of furfural in the transformer oil and the degree of polymerization representing the degree of aging of the insulating paper, and can be expressed as an exponential function as shown in (2).

\[
\log(F_a) = 1.51 - 0.0035D
\]  

(2)

Where \( F_a \) represents the furfural concentration and \( D \) represents the degree of polymerization of insulating paper.

As the running time of the transformer increases, the content of furfural in the insulating oil also increases, and the two have a linear relationship as follows.

\[
\log(F_a) = -1.31 + 0.05T
\]  

(3)

In (3), \( T \) represents the running years of the transformer.

According to the results of many years of observation, when the content of furfural in the oil exceeds Tab. 6, it is generally abnormal aging, which needs to be followed up. When tracking detection, pay attention to the growth rate. When the test value is greater than 4mg/L, the insulation aging is considered to be serious.

**Table 6.** Controllable furfural contents in oil.

| Operation years | 1~5 | 5~10 | 10~15 | 15~20 |
|-----------------|-----|------|-------|-------|
| Furfural contents(mg/L) | 0.1 | 0.2 | 0.4 | 0.75 |

When the oil with a long operating period is found to have a large or rapid increase in furfural content in the oil, a comprehensive judgment should be made. If it is suspected that the insulation paper is aging, the degree of polymerization of the insulating paper should be checked again, and judged based on the test results.

5. Transformer aging analysis

The test of furfural content in transformer oil can not only visually reflect the degree of overheating aging of transformer insulation paper, but also diagnose latent faults involving solid insulation materials. With the in-depth study of the furfural test method and the continuous accumulation of a large amount of analytical data, judging the solid insulation condition of the transformer according to the analysis of furfural content in the oil will become one of the important means of power transformer operation supervision. It is an inevitable trend of power development to evaluate the operating condition of transformers by using furfural content in oil.

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