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Application of Secondary Degassing Method in Detection of Dissolved Gas Components in insulating Oil

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Abstract. In the test of dissolved gas components in insulating oil, if the oil sample has been degassed but the test failed due to other reasons, the principle of the distribution of each gas component in the oil can be applied to calculate component content. The degassed oil sample is filled with blank balance gas and tested again. After the test results are corrected, the original concentration of each component in the oil sample can be obtained. This method simple and reliable, reduced the trouble of repeated sampling.

1. Introduction
In the maintenance and repair of power systems, the dissolved gas components in the oil has been widely used because it can be reflected the operational health of oil-filled equipment, and the important position of dissolved gas in transformer failure is emphasized [1] in DL/T 596 “Preventive test code for electric Power equipment”. Gas chromatography is the most accurate and widely used method for detecting the content of gas components in oil, but test process is cumbersome and some reasons can cause the test failure, such as sudden malfunction or power failure of the chromatograph, gas leakage during injection. Usually, such cases can only be re-sampled, which bring lots of inconvenience to the work.

At present, the degassing of oil samples mostly adopts the mechanical oscillation method. Through the analysis of the test principle of this method, find the secondary degassing test can be carried out by adding the carrier gas to the degassed oil sample again. Appropriately corrected the secondary degassing test results, the actual content of the components of the dissolved gases in the oil can still be obtained. This method simple and convenient, and a large number of experiments also be proved that the test result is true and reliable.

2. Experimental principle and formula revision
Through the analysis of the experimental principle of the mechanical oscillation method, according to the distribution coefficient and the material balance principle, formula (1) and (2) are established.

\[ K_i = \frac{C_{il}}{C_{ig}} \quad \text{(or} \quad C_{il} = K_i \cdot C_{ig} \text{)} \]  

(1)
\[ X_i = C_{ig} \left( K_i + \frac{V_g}{V_1} \right) \]  

(2)

Among them, \( K_i \) is partition coefficient of dissolved gas component \((i)\) after gas-liquid two-phase equilibrium at test temperature;

\( C_{il} \) is concentration of dissolved gas component \((i)\) in liquid under equilibrium conditions, \( \mu L/L \);

\( C_{ig} \) is concentration of dissolved gas component \((i)\) in gas under equilibrium conditions, \( \mu L/L \);

\( X_i \) is concentration of dissolved gas component \((i)\) in oil sample, \( \mu L/L \);

\( V_g \) is gas volume under equilibrium conditions, \( mL \);

\( V_1 \) is liquid volume under equilibrium conditions, \( mL \);

Formula (1) is the Distribution Law. This law can be described as follow: Under certain temperature and pressure conditions, the ratio of the concentration of the dissolved gas component \((i)\) in the liquid phase to its concentration in the gas phase is constant when the equilibrium state is reached.

Since \( K_i \) is a fixed value [2] (shown in Table 1), as long as the concentration of component\((i)\) \( C_{ig} \) in the gas under equilibrium conditions is detected by the chromatograph, its content in the liquid \( C_{il} \) can be obtained according to Distribution law. The concentration, which in turn can be derived, is used to calculate the concentration of the dissolved gas component \((i)\) in the oil. Furthermore, the concentration of the dissolved gas component \((i)\) \( X_i \) in the oil can be obtained.

It can be found from the principle of the Distribution Law that the degassing test is performed again on the oil sample which had been degassed, formula (1) and (2) are still valid. When the oil sample is tested by secondary degassing, there is:

\[ X'_i = C_{ig} \]  

(3)

\( X'_i \) is the concentration of the component\((i)\) in the oil sample measured after the second degassing test, equal to the concentration of the component\((i)\) remaining in the oil sample after the first degassing.

Substituting formula (3) into (1) and sorting,

\[ C_{ig} = \frac{C_{il}}{K_i} = \frac{X'_i}{K_i} \]  

(4)

Substituting formula (4) into (2) gives the correction formula:

\[ X_i = \frac{X'_i}{K_i} \left( K_i + \frac{V_g}{V_1} \right) = X'_i \left( 1 + \frac{V_g}{K_i V_1} \right) \]  

(5)

Among them, \( V_g \) is gas volume under equilibrium conditions for the first degassing, \( K_i \) and \( V_1 \) remain unchanged in the two degassing experiments before and after. Therefore, as long as the volume of the equilibrium gas \( V_g \) at the first degassing test is known, the degassed oil sample can be
degassed again. The test result after the second degassing \( X'_i \) can be corrected by formula (5), and the corrected result \( X_i \) is the concentration of component (i) in the original oil sample.

Table 1. Partition coefficient of dissolved gases in oil at 50°C.

| Partition Coefficient | \( H_2 \) | \( CH_4 \) | \( C_2H_6 \) | \( C_2H_4 \) | \( C_2H_2 \) | \( CO \) | \( CO_2 \) |
|-----------------------|-----------|-----------|-----------|-----------|-----------|-------|-------|
| \( K_i \)             | 0.06      | 0.39      | 2.30      | 1.46      | 1.02      | 0.12  | 0.92  |

3. Experimental demonstration of secondary degassing method

Two 40 mL oil samples (represented by #1 and #2) were tested at room temperature. Taking the #1 sample as an example, the test procedure is as follows: Firstly, add 5 mL of carrier gas (nitrogen) to the oil sample. After the first balance at 50°C, remove the degassed gas and accurately read the degassing volume \( V_{g1} \); Then, a carrier gas is injected into the degassed oil sample for secondary degassing. Chromatographic analysis of the two gases removed by chromatograph to obtain the actual concentration of component (i) in the oil and the concentration after secondary degassing \( X'_i \); calculate the actual concentration of component (i) \( X_i \) in oil by formula (5). Compare the inverse and actual values, verify the test accuracy of the secondary degassing method.

The first degassing volume \( V_{g1} \) of #1 sample is 5mL, and the detection spectrum is shown in Figure 1. The detection spectrum after secondary degassing is shown in Figure 2. The specific values and comparisons are shown in Table 2.

![Detection spectrum of #1 Sample after first degassing](image1)

(a) FID detector (b) TCD detector.

![Detection spectrum of #1 Sample after second degassing](image2)

(a) FID detector (b) TCD detector.
Similarly, the first degassing volume $V_{g1}$ of #2 sample is 4.5mL, and the detection spectrum is shown in Figure 3. The detection spectrum after secondary degassing is shown in Figure 4. The specific values and comparisons are shown in Table 3.

![Figure 3](image1.png)  
(a) FID detector (b) TCD detector.

![Figure 4](image2.png)  
(a) FID detector (b) TCD detector.

### Table 2. #1 sample chromatographic data.

| Component(i) | $H_2$ | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_2H_2$ | CO | $CO_2$ |
|--------------|-------|--------|----------|----------|----------|----|--------|
| $X_i$ (μL/L) | 73.43 | 30.3   | 32.98    | 30.49    | 3.47     | 261.38 | 1906.2 |
| Actual value(μL/L) | 21.72 | 21.78 | 29.66 | 26.87 | 2.95 | 121.4 | 1519.82 |
| Relative deviation (%) | 9.2 | 5.2 | 5.3 | 4.4 | 4.7 | 5.3 | 9.9 |

It can be found from Table 2 and Table 3, the inverse value by secondary degassing method is very close to the actual value. The relative deviation between the two meets the requirements for repeatability $r$ in GB/T 17623-2017.

### Table 3. #2 sample chromatographic data.

| Component(i) | $H_2$ | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_2H_2$ | CO | $CO_2$ |
|--------------|-------|--------|----------|----------|----------|----|--------|
| $X_j$ (μL/L) | 17.48 | 7.62   | 8.62     | 8.0      | 0.82     | 87.3 | 813.79 |
| Actual value(μL/L) | 19.15 | 7.98 | 8.75 | 8.1 | 0.83 | 87.55 | 850.04 |
| Relative deviation (%) | 9.1 | 0.7 | 1.5 | 1.2 | 1.0 | 0.3 | 4.4 |
4. Precautions
1) When applying the secondary degassing method, the mechanical oscillation method should be applied correctly. During the experiment, the test requirements should be strictly observed to reduce the test error.

2) In the mechanical oscillation degassing step of the secondary degassing method, it is important to correctly read the volume of the first degassed gas. Because it can be found from formula (5) that the first balance degassing volume plays a decisive role in calculating the actual concentration of the components.

5. Conclusion
The test shows that the component (i) in the oil sample by formula (5) is very close to the actual value, which indicates that the application of the secondary degassing method in gas chromatography analysis is feasible. This method can not only solve the difficulty of repeated sampling due to test failure, but also verify the authenticity of the test data.

However, this method is generally not suitable for the new oil test because the concentration of each component in the new oil is relatively low, and the inverse value of the secondary degassing method often has a large difference from the actual value.

References
[1] DL/T 596-1996 Preventive test code for electric Power equipment[S].
[2] GB/T 17623-2017 Determination of componental contents of gases dissolved in insulating oil by gas chromatography method[S].