The detection of dissolved gases in transformer oil by gas chromatography with helium ionization detector

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Abstract. The GC-PDD with the technology of valve cutting and helium ionization detector was used to analyze the dissolved gases in ultra-high voltage (UHV) and extra-high voltage (EHV) transformer oil. The detection limit (DL) reached ppb grade, especially for the featuring gas—C₂H₂ and H₂, whose DL could reach 5 ppb and 11 ppb respectively. The test reproducibility of the instrument was about 1% and the correlation coefficient of standard curve-r is greater or equal to 0.99, which showed obvious advantage compared with normal GC. In addition, the auxiliary gas of H₂ was not used in this instrument, which completely improved the safety performance. Thus, the application of GC-PDD has significant meaning in warning potential malfunction inside the ultra-high voltage transformer in advance.

1. Introduction

With the continuous development and progress of power system, ultra-high voltage transmission of electricity is becoming more and more extensive. And the safe and reliable operation of UHV and EHV transformer equipment plays a very important role in the reliability of urban power supply system. At present, a large number of domestic EHV transformers are easy to cause larger accidents due to higher voltage, micro-discharge and overheating, so that higher requirements are put forward for prevention and detection of early accidents of dissolved gases in transformer oil. So the requirement for instrument detection limit is higher, the application of traditional chromatography is unable to meet the requirements for analysis[1].

Dissolved gases in the transformer oil include hydrogen, methane, ethane, ethylene, acetylene, carbon monoxide and carbon dioxide. In the early stage of fault, the gas formed is dissolved in oil; when the energy of fault is large, it may also gather into free gas[2,3]. Therefore, it is of great significance to periodically measure the composition and content of gases dissolved in oil for the early detection of the potential faults inside oil-filled power equipment. In order to avoid the misunderstanding of electrical equipment failure, IEC 60567[4] and IEC 60599[5] had put forward specific requirements for the test cycle and the detection methods.

In current IEC standard, dissolved gases had been separated from the oil by headspace gas taking or shock separation. In the IEC detection method, two kinds of detectors and a chemical conversion device should be applied. Han Yuwang had detected dissolved gas with AC pulse helium ionization detector, which proofed the applicability of this detector[6]. J. Jalbert, R. Gilber, and P. Te’ treault have ever detected the dissolved gases by headspace degassing method with helium ion-detector gas chromatograph and proofed a higher detection limit and enhanced space[7]. In this paper, helium ionization detector was chosen too. Helium ionization detector is a universal detector, especially for especially for trace gases. The helium ion gas chromatograph was proposed, which can not only simplify the chromatographic process but also improve detection sensitivity.
2. Experimental part

2.1. New GC-9560-PDD helium ionization gas chromatograph
Hereinafter referred to as GC-9560-PDD; Shanghai Hua’ai Chromatography Analysis Co. Ltd is equipped with helium purifier and helium ionization detector and its process is converted to double 10-way valve switching process as shown in Figure 1. Injector used is a packed column injector; carrier gas is purged by control of on-off valve. Nitrogen is used as valve-driving gas and usual gas taking port design like ordinary transformer oil instrument is used as gas taking port. Four-way valve seal the system is adopted.

2.2. Traditional GC-9560-HD gas chromatograph
Hereinafter referred to as GC-9560-HD; Shanghai Hua’ai Chromatography Analysis Co. Ltd is equipped with thermal conductivity detector and dual hydrogen flame detector with the process of IEC three detectors as shown in Figure 2.

Figure 1. Flow chart of GC-9560-PDD

Figure 2. Flow chart of GC-9560-HD
2.3. Standard gases
Standard gases (certificate number:15-09680) was Made by Shanghai Weichuang Standard Gas Co., Ltd. The density value of standard gas was shown in Table1. High-purity helium (99.999%) and High-purity nitrogen (99.999%) was made by Shanghai Pujiang Gas Co., Ltd.

Table 1. The component of standard gas.

| Component | Content (10⁻⁶/V/V) | Component | Content (10⁻⁶/V/V) |
|-----------|--------------------|-----------|--------------------|
| CH₄       | 101                | C₂H₂      | 50.0               |
| C₂H₆      | 99.4               | H₂        | 985                |
| C₂H₄      | 99.3               | CO        | 1014               |
| CO₂       | 2993               | N₂        | rest               |

3. Results and discussion

3.1. Flow of new instrument
As shown in Figure 1, GC-9560-PDD has gone through a large number of experiments and continuous improvement and is pre-division of column Q, which guides hydrogen, oxygen, nitrogen, methane and carbon monoxide into column 5A. Column 5A will separate hydrogen, oxygen, nitrogen, methane and carbon monoxide, in which, hydrogen peak is first-out before switching to another column GDX-502, carbon dioxide, ethylene, ethane and acetylene emerge then column Q, and detector switches to 5A, this moment, oxygen and nitrogen have been vented before methane and carbon monoxide peaks emerge. It takes 7 minutes for one injection of spectrogram. Figure 3 is a typical spectrogram of standard gas.

3.2. Comparison of new instrument with IEC process
Figure 4 is a chromatogram of GC-9560-HD. The chromatographic instrument used three detectors, included a thermal conductivity detector and two hydrogen flame ionization detectors. Thermal conductivity detector is used to detect hydrogen, hydrogen flame ionization detector to detect carbon monoxide and carbon dioxide which are converted to methane by reformer, and another way to detect the hydrocarbons such as methane, ethane, ethylene and acetylene. This method wants more detectors, in which hydrogen is used as auxiliary gas; in case of explosion, risk is higher. And the new GC-9560-PDD only needs helium as carrier gas, with nitrogen gas as auxiliary gas so as to greatly improve safety because both the gases are inert gases.

![Figure 3. Typical chromatogram of standard gas by GC-9560-PDD](image-url)
3.3. Precision of the new instrument

Table 2 shows the repeatability of GC-9560-PDD in measuring the peak area of standard gases. Test repeatability of the instrument was less than 1%. It was indicated that the precision of the method satisfy test requirement.

3.4. Detection limit of seven gases on the new instrument

The theoretical detection limit of chromatograph was known as the short baseline noise of the instrument within 30 minutes, and the baseline noise is taken as the detection limit of 3 times, as shown in Formula1.

\[ D = \frac{3 \times N \times Q}{I} \]  

(1)

Table 3 shows the comparison between BG detection limit, the theoretical detection limit (hereinafter known as DL) of GC-9569-HD and GC-9560-PDD. It can be found that GC-9560-HD meet IEC 60599, the theoretical DL of GC-9560-PDD is nearly 80 times higher than GC-9560-HD, and other gases over 5 times. The DL of C2H2 reached 5 ppb, which gives the greatest impact on fault judging.

Table 2. Repeatability test of standard gases by GC-9560-PDD

| Component | H2  | CO2 | C2H4 | C2H2 | C2H6 | CH4 | CO  |
|-----------|-----|-----|------|------|------|-----|-----|
| 1st time  | 459061 | 4094160 | 6555893 | 905922 | 250753 | 452624 | 157970 |
| 2nd time  | 459647   | 4120209 | 6689060 | 924290 | 257206 | 458963 | 159275 |
| 3rd time  | 456684   | 4102020 | 6665540 | 921890 | 256381 | 456000 | 157710 |
| 4th time  | 454744   | 4094985 | 6653227 | 920158 | 256142 | 452165 | 155722 |
| 5th time  | 453464   | 4074167 | 6612642 | 913672 | 254301 | 450146 | 155837 |
| 6th time  | 458616   | 4087308 | 6648826 | 918631 | 255151 | 453631 | 156945 |
| AVERAGE   | 457036   | 4095475 | 6637531 | 917427 | 255151 | 453631 | 156945 |
| RSD       | 0.55%   | 0.37% | 0.71% | 0.73% | 0.92% | 0.71% | 1.03% |
Table 3. The comparison of DL

| Component           | H₂      | CH₄     | CO₂     | C₂H₄    | C₂H₂    | C₂H₆    | CO     |
|---------------------|---------|---------|---------|---------|---------|---------|--------|
| DL in IEC 60599     | ≤2      | /       | ≤25     | /       | ≤0.1    | /       | ≤25    |
| DL of GC-9560-HD (10⁻⁶V/V) * | 0.88    | 1       | 0.99    | 7       | 0.03    | 0.046   | 0.037  | 0.273  |
| DL of GC-9560-PDD (10⁻⁶V/V) ** | 0.01    | 0.005   | 0.01    | 1       | 0.003   | 0.005   | 0.003  | 0.041  |

Note: *The noise of the data is 4 μV
**The noise of this data is 20μV

3.5. Linearity of the new instrument to seven gases

Figure 5 shows the standard curve spectrogram of H₂ after dilution of the standard gases of different multiples, a standard curve got at the lowest concentration of 1.97 × 10⁻⁶ to 985 × 10⁻⁶, with the linear dependency R² of 0.9965. Figure 6 shows the standard curve spectrogram of CO₂ after dilution of the standard gases of different multiples, a standard curve got at the lowest concentration of 5.99 × 10⁻⁶ to 2993 × 10⁻⁶, with the linear dependency R² of 0.9939. Figure 7 shows the standard curve spectrogram of ethylene after dilution of the standard gases of different multiples, a standard curve got at the lowest concentration of 0.199 × 10⁻⁶ to 99.4 × 10⁻⁶, with the linear dependency R² of 0.9996. Figure 8 shows the standard curve spectrogram of ethene after dilution of the standard gases of different multiples, a standard curve got at the lowest concentration of 0.199 × 10⁻⁶ to 99.3 × 10⁻⁶, with the linear dependency R² of 0.9997. Figure 9 shows the standard curve spectrogram of acetylene after dilution of the standard gases of different multiples, a standard curve got at the lowest concentration of 0.10 × 10⁻⁶ to 50.0 × 10⁻⁶, with the linear dependency R² of 0.9972. Under the low concentrations of 0.1 ppm, peaking is still up to 2900 μV, showing a good peaking at low concentrations. Figure 10 shows the standard curve spectrogram of methane after dilution of the standard gases of different multiples, a standard curve got at the lowest concentration of 0.20 × 10⁻⁶ to 101.0 × 10⁻⁶, with the linear dependency R² of 0.9970. Figure 11 shows the standard curve spectrogram of carbon monoxide after dilution of the standard gases of different multiples, a standard curve got at the lowest concentration of 2.2 × 10⁻⁶ to 1014 × 10⁻⁶, with the linear dependency R² of 0.9977.

Through the linear experiment, it is found that within 500 times of diluted standard gases, there is still a good linear on the instrument, no way to be diluted to lower concentration, well consistent with the result of headspace method helium ion chromatography made by J. Jalbert, R. Gilber and P. Te’treault, with a good linear [7].
4. Conclusion
A new type of helium ionization gas chromatography with helium ionization detector has been reported for the first time. Test result indicated that it can be used to separate and detect 7 kinds of dissolved gas in transformer oil within 7 minutes. The advanced nature of the instrument is reflected in the detection limit. Detection limit is increased nearly 80 times higher than the detection limit H₂ by traditional GC-9560-HD gas chromatograph, increased over 5 times than other gases. The C₂H₂ which has the greatest impact on the determination of fault has reached a detection limit of 5 ppb. The test reproducibility of the instrument was about 1%. The correlation coefficient of standard curve-r is greater or equal to 0.99. The ultra-low detection limit provided a better platform for the early prevention and fault diagnosis of extra-high voltage transformers. In addition, because of the absence of hydrogen, the safety is quantitatively improved.
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