Method for the Determination of Decomposition Products in New Eco-friendly CF$_3$I-N$_2$ Mixture

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Abstract. During the operation of GIS, any fault of GIS may cause partial discharge; when the new eco-friendly CF$_3$I-N$_2$ mixture is applied to GIS, it will also decompose under discharge conditions; at present, there are some researches on the decomposition products of CF$_3$I gas at home and abroad; under DC voltage, CF$_3$I-N$_2$ mixture will discharge to produce by-products mainly including C$_2$F$_6$ and C$_2$F$_5$I; we can infer the running state of the equipment by determining the content of these impurities, while the determination method for this gas is still blank; this paper proposes a gas chromatography scheme through experimental research, and a chromatographic column and chromatographic operating condition optimization experiment was carried out to establish a chromatographic method for the determination of impurities in CF$_3$I-N$_2$ mixture.

1. Introduction

Gas-insulated electrical equipment usually adopts sulfur hexafluoride gas (SF$_6$) as the insulating medium. However, due to the strong greenhouse effect of SF$_6$, its GWP value is about 23,900 times of that of CO$_2$ [1], which hinders the green development of China’s power grid and even the global power grids. Therefore, to search out a kind of eco-friendly substitute gas for SF$_6$ with equivalent electrical performance has become a research hot spot at home and abroad in recent years. CF$_3$I has become one of good substitute gases by virtue of its excellent performance. CF$_3$I is colorless, odorless, non-toxic and non-combustible. Its GWP (Global Warming Potential) value is less than 5, ODP (Ozone Depletion Potential) value is basically 0, and it has excellent insulating property. Since the high liquefaction temperature of CF$_3$I can reach 25°C under the operating pressure of existing electrical equipment, it cannot be used directly in power equipment. CF$_3$I liquefaction temperature can be reduced by adding buffer gas like N$_2$ to make it applicable to power equipment [2]. Research shows the insulating strength of pure CF$_3$I is 1.2 times of that of SF$_6$ in a slightly non-uniform field, while the breakdown voltages of CF$_3$I-N$_2$ mixture and CF$_3$I/air mixture increase linearly with the content of CF$_3$I in the mixed gas. In mixed gas CF$_3$I/N$_2$, when the CF$_3$I content accounts for 60%, the insulating strength of CF$_3$I-N$_2$ mixture is equivalent to that of pure SF$_6$ [3].

At present, there are some researches on the decomposition products of CF$_3$I at home and abroad [4-6]. Under DC voltage, CF$_3$I-N$_2$ mixture will discharge to produce by-products mainly including C$_2$F$_6$ and C$_2$F$_5$I, and the running state of the equipment can be inferred by determining the content of these impurities, while the determination method for this gas is still blank. This paper proposes a gas
chromatography scheme through experimental research, and a chromatographic column and chromatographic operating condition optimization experiment was carried out to establish a chromatographic method for the determination of impurities in CF3I-N2 mixture.

2. Experimental method

2.1 Standard gas configuration

Although there is no specific report on the discharge decomposition products of CF3I-N2 in China, research shows CF3I will discharge to produce C2F6 and C2F5I [7], and these two impurities are characteristic impurities of discharge. Therefore, they must be included in the key component analysis objects. Besides, since the existing H2O and N2 may react with CF3I, it’s necessary to include the following impurities in the analysis and configure the standard gas according to these impurity components.

| Component  | H2O  | O2 | CO | CH4 | CF4 | CO2 |
|------------|------|----|----|-----|-----|-----|
| C (ppm)    | 4.9  | 3.3| 4.6| 4.7 | 5.1 | 5.1 |

| Component  | N2O | CHF3 | C2F6 | C2F5I | N2 | He   |
|------------|-----|------|------|-------|----|------|
| C (ppm)    | 4.7 | 4.7  | 5.3  | 6.3   | 30%| Balance |

2.2 Design of chromatographic process

In this paper, gas chromatograph with helium ionization detector is adopted to analyze the decomposition products. Due to the existence of the main components N2 and CF3I, the process design must be realized by means of cutting and venting. A helium ionization detector is used via the single channel. The back flushing impurities of analysis column 1 are vented through needle valve 1. Column 2 is for analysis of H2, O2 and CO, and N2 is vented through needle valve 2. Analysis columns 3 and 4 are for the analysis of CH4, CF4, N2O, CO2, CHF3, C2F6 and C2F5I, N2 and CF3I are vented through needle valves 3 and 4. During the analysis of C2F5I, the temperature of column 3 is increased, and the analysis is completed.


3. Standard gas analysis

3.1 Standard gas chromatogram

Reproducibility is expressed as the relative standard deviation (RSD) of the retention time, peak height and peak area measurements of the components. The RSD is calculated by the formula below:

\[
RSD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{(n-1)}} \times \frac{1}{\bar{x}} \times 100\%
\]

Wherein: RSD refers to relative standard deviation (%); n refers to the number of measurements; \(x_i\) refers to the retention time, peak height or peak area of the i\(th\) measurement; \(\bar{x}\) refers to the arithmetic mean value of retention time, peak height or peak area of the nth sample injection; and i refers to the injection number.

The experiment is conducted 7 times under the analysis conditions of Fig. 1 to obtain the following data table (Table 3): the unit of peak height is uv, the unit of peak area is \(\mu V\times s\), and the unit of retention time is s; the results show that the reproducibility by this method is within 3%, which fully meets the requirements of verification analysis.

![Fig.2. Standard Gas Chromatogram](image-url)

| Component | 1  | 2   | 3   | 4   | 5   | 6   | 7 Mean Value | RSD |
|-----------|----|-----|-----|-----|-----|-----|-------------|-----|
| \(H_2\) Peak | 30163 | 49923 | 50602 | 49732 | 50031 | 50821 | 50661 | 50276.1 | 0.83% |
| Area | 88857.0 | 88431.9 | 89634.6 | 88093.5 | 88623.2 | 88921.3 | 88320.7 | 88697.5 | 0.27% |
| Retention time | 0.495 | 0.499 | 0.493 | 0.497 | 0.492 | 0.495 | 0.493 | 0.495 | 0.50% |
| \(O_2\) Peak | 31402 | 31021 | 31550 | 30928 | 31222 | 31669 | 31598 | 31341.4 | 0.93% |
| Area | 57984.4 | 57280.9 | 58257.7 | 57109.1 | 57652.0 | 58477.4 | 58300.0 | 57865.9 | 0.92% |
| Retention time | 0.895 | 0.894 | 0.893 | 0.896 | 0.898 | 0.899 | 0.893 | 0.895 | 0.26% |
| \(CO\) Peak | 21059 | 21000 | 21138 | 20973 | 21032 | 21199 | 21166 | 21081.0 | 0.41% |
| Area | 214721.1 | 214119.5 | 215526.6 | 213844.2 | 214445.8 | 216448.6 | 216080.0 | 214973.4 | 0.43% |
| Retention time | 3.265 | 3.264 | 3.266 | 3.266 | 3.269 | 3.270 | 3.268 | 3.267 | 0.07% |
| \(CF_4\) Peak | 41825 | 41632 | 42301 | 40521 | 41321 | 43021 | 41831 | 41778.9 | 1.86% |
| Area | 295373.5 | 294010.5 | 298735.1 | 286164.5 | 291814.2 | 303819.8 | 297213.0 | 295304.4 | 1.88% |
| Retention time | 4.525 | 4.525 | 4.528 | 4.530 | 4.530 | 4.527 | 4.529 | 4.528 | 0.05% |
| \(CH_4\) Peak | 117804 | 117600 | 117969 | 117503 | 117621 | 122300 | 117995 | 118398.9 | 1.46% |
| Area | 768597.6 | 767266.6 | 769674.1 | 766633.8 | 767403.6 | 783212.0 | 755642.7 | 768347.2 | 1.03% |
| Retention time | 4.715 | 4.714 | 4.710 | 4.721 | 4.722 | 4.719 | 4.715 | 4.720 | 0.11% |
| \(CO_2\) Peak | 699373.5 | 692498.5 | 699538.4 | 692317.1 | 694542.8 | 705176.9 | 688212.1 | 695951.3 | 0.82% |
| Area | 424220 | 42003 | 42439 | 41992 | 42127 | 42772 | 42550 | 42327.7 | 0.70% |
| Retention time | 6.765 | 6.766 | 6.770 | 6.772 | 6.770 | 6.772 | 6.758 | 6.768 | 0.07% |
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3.3 Limit of detection (LOD)

Evaluation of chromatographic method requires detection of the LOD. Since the helium ionization detector is a concentration type detector, calculate its volume LOD by the formula below:

\[ D = \frac{3NVc}{AF} \times 10^3 \]

Wherein: D/volume LOD (ppb); N/noise (μV); V/volume of sample loop tube (mL); c/component concentration (ppm); A/peak area (μV×s); F/corrected flow (mL/s); H/peak height (μV);

Table 3. LOD of Various Components in Standard Gas

| Component | H₂ | O₂ | CO | CH₄ | CF₄ |
|-----------|----|----|----|-----|-----|
| c(ppm)    | 4.9| 4.3| 4.6| 4.7 | 5.1 |
| A(uV·s)   | 88857.0| 57984.4| 214721.1| 768597.6| 295373.5|
| D(ppb)    | 3.3| 4.4| 1.2| 1   | 3.3 |

| Component | CO₂ | N₂O | CHF₃ | C₂F₆ | C₂F₅I |
|-----------|-----|-----|------|------|-------|
| c(ppm)    | 5.1| 4.7| 4.7  | 5.3  | 6.3   |
| A(uV·s)   | 699373.5| 586580.5| 768515.3| 1005123.8| 775491.4|
| D(ppb)    | 1.3| 1.7| 1.3  | 1    | 1.7   |

In this experiment: the volume of the sample loop tube 1 is 0.5ml; the volume of the sample loop tube 2 is 1ml; the corrected flow F₁ is 0.5mL/s, and F₂ is 0.3mL/s; the baseline noise is 20μV; based on the data given in Table 3, we calculated the volume LOD for each component below (Table 4). By using standard gas results, we calculate the LOQ according to 3 times of the noise (20μv), as shown in Table 4. Through the analysis of the standard gas, the volume LOD by this method is below 10ppb, which meets the detection requirements of CF₃I-N₂.

3.4 Linearity

In this experiment, the dynamic gas distribution system is adopted to dilute the standard gas by 5, 20, 50, and 100 times respectively. Then, chromatographic analysis is conducted on the diluted standard gas, and a fitting curve is made by the use of a chromatographic work station to verify its linearity. The results are shown in Fig. 3-12 below. Through experimental verification, the R² value of the calibration curve for each component of the standard gas is greater than 0.999, and the linearity is good, which meets the analysis requirements.
Fig. 3. Linearity of H$_2$

Fig. 4. Linearity of O$_2$

Fig. 5. Linearity of CO

Fig. 6. Linearity of CF$_4$

Fig. 7. Linearity of CH$_4$

Fig. 8. Linearity of CO$_2$
4. Sample analysis

4.1 Data of results

In this experiment, chromatographic analysis is conducted on the sample of CF3I-N2 mixture to obtain the following data (Fig. 13 and Table 4).
4.2 Discussion of results

a) In the standard gas analysis, all components can be completely separated, and the LOQ of each impurity is about 20ppb, which fully meets the analysis requirements of CF3I-N2 decomposition products.

b) We detect the CF3I-N2 mixture after discharge. Among the components, the concentration of the main fluoride CF₄ is 4ppm, that of C₂F₆ is 4.15ppm, that of CHF₃ is 0.62ppm, and that of C₂F₅I is 0.13ppm. Based on the analysis of the above experimental results, we infer that the discharge decomposition of CF3I-N2 can be expressed by the following expressions:

\[ \text{CF}_3\text{I} \xrightarrow{\text{Discharge}} \text{CF}_3 \cdot + \text{I} \cdot \]
\[ \text{CF}_3 \cdot + \text{CF}_3 \cdot \rightarrow \text{C}_2\text{F}_6 \]
\[ \text{CF}_3 \cdot \xrightarrow{H_2O} \text{CHF}_3 \]
\[ \text{CF}_3 \cdot + \text{CF}_3 \text{I} \rightarrow \text{C}_2\text{F}_5\text{I} + \text{CF}_4 \]
\[ \text{I} \cdot + \text{I} \cdot \rightarrow \text{I}_2 \]

c) From the above expressions, due to the existence of \( \text{I} \cdot \), we infer that there may be solid I₂ in the sample, and the specific reaction formula is as follows:

5. Conclusion

In case of discharge, the main impurities of the new eco-friendly gas CF3I-N2 are CF₄, C₂F₆ and CHF₃, and the generation of these impurities will reduce the insulating strength of the mixed gas. Therefore, it is necessary to determine the decomposition products of CF3I-N2 mixture. In this paper, the method for the determination of decomposition products in the new eco-friendly gas CF3I-N2 is established, and the reproducibility, LOD and linearity by the method are verified. According to the results, the reproducibility is within 3%, the LOD is below 50ppb, and the linearity is above 0.999, meeting the analysis requirements of CF3I-N2 mixture. When the eco-friendly gas CF3I-N2 is applied to GIS, this experiment can be regarded as a basis for judging the running state of GIS. It also provides reference value and evaluation methods for the discharge mechanism of eco-friendly SF₆ substitute gas, as well as other relevant theoretical researches.

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