Concentrated injection method for the improved sensitivity in detecting the decomposed products of SF₆

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Abstract. A concentrated injection method for detecting SO₂, H₂S, SO₂F₂ and SOF₂ in sulfur hexafluoride (SF₆) based on Gas Chromatography-Mass Spectrometer (GC-MS) measurements has been proposed and developed. The peak intensity of the component obtained by concentrated injection method for detecting 1 μL/L SO₂ was 20 times larger than that estimated by ordinary injection method, indicating a higher sensitivity, and a lower detection limit as well. This work shows advantages for the pre-warning of pitfall in electrical equipment, and effectively improves the safety and reliability of the grid.

1. Introduction

Sulfur hexafluoride (SF₆) based electrical equipment has been extensively used in high-voltage electrical equipment, owing to the limited size, high reliability, and ease of maintenance. Generally, SF₆ is a good insulator with a high stability without releasing decomposed products [1,2]. However, the internal insulation material will be decomposed when there are internal overheating and discharge failures, accompanying the formation of dozens of derivatives such as sulfur tetrafluoride (SF₄), sulfur dioxide (SO₂), thionyl fluoride (SOF₂), hydrogen sulfide (H₂S), sulfuryl fluoride (SO₂F₂), thionyl fluoride (SO₄), sulfur pentafluoride (S₂F₁₀), sulfur dioxide decaoxide (S₂OF₁₀) and hydrogen fluoride (HF) [3,4]. One of the most effective techniques for diagnosing internal breakdown of SF₆ based electrical equipment is the identification of characteristic derivatives and the detection and analysis of the content change [5,6].

The chromatographic method is commonly used for the detection of decomposed products in SF₆ at current stage. However, challenges still exist in the ordinary chromatographic method, since some decomposition products cannot be detected. It can be attributed to the poor detection limit and the similar retention time of the impurity components due to the close boiling points compared with that of the SF₆. Therefore, it is eagerly to improve the detection sensitivity for the decomposed products of SF₆. The method of freeze concentration has gradually been introduced into the field of SF₆ decomposition products analysis. The concentration of the impurity components to be measured can be increased by an order of 10-1000 times with the concentrated injection method, which can satisfy the detection ability of the vast logarithmic gas chromatographic detector.

In this work, low-temperature enrichment method was used for concentrating the decomposition products, and the concentrated samples were analyzed by chromatography.
2. Experimental details
The SF$_6$ decomposition products were analyzed by Gas Chromatography-Mass Spectrometry (GC-MS) with a three cooling functions of concentrated sampling device. The detector is non-polar capillary column and electron bombardment source (EI). The cooling medium is liquid nitrogen. The carrier gas is helium (or hydrogen) with the purity of 99.999%.

The resolution of all components can meet the requirements of quantitative analysis. A CP-Sil 5 CB capillary column with a length of 60 m, a film thickness of 8 μm, and an inner diameter of 0.32 mm were used for the experiments. Prior to use, the temperature of new column should be increased to 250 °C with a speed of 5-6 °C / min by a controlled program, then it was repeated several times. The temperature was further increases to 280 °C, and was repeated several times. The baseline increased to normal situation when the temperature is higher than 270 °C. Then the new column was reaged to 300 °C for half an hour.

The mass percentage of single-component gas and multi-component mixed gas are greater than 50% of the corresponding unknown component content, or less than 30% of the unknown component content. The standard gases used in this work are: (1) SO$_2$F$_2$ standard gas: 50.3 × 10$^{-6}$ mol/mol, He is the bottom gas; (2) SOF$_2$ standard gas: 50.1 × 10$^{-6}$ mol/mol, He is the bottom gas; (3) SO$_2$ standard gas: 9.8×10$^{-6}$ μL/L, SF$_6$ is the bottom gas; (4) H$_2$S standard gas: 40.6×10$^{-6}$ μL/L, SF$_6$ is the bottom gas.

3. Results and discussion
3.1 The optimization of the concentrated injection conditions
The gas sample is subjected to a three-stage refrigeration concentration test by a gas concentrator. The most of the decomposition products can be separated from the SF$_6$ and the H$_2$O during the first-stage refrigeration, and the detection can be effectively enhanced. Then, the decomposed products can be further concentrated via the second stage of refrigeration. After that, the decomposition products would be more concentrated after the third-stage of refrigeration, and the accuracy for the detection of decomposed products can be effectually improved. The temperature of the cooling trapping and desorption can be optimized for each stage.

3.2 Optimizing the first-stage of cooling temperature

![Figure 1 Select ion map of standard gas at 0.1 μL/L sulfur dioxide at different primary refrigeration temperatures.](image)
Among the decomposition products of SF₆, SO₂ is considered to be a stable derivative released during breakdown of the equipment. It is reasonable and reliable to judge the situation by detecting the concentration of SO₂. As an example, the effect of refrigeration conditions on the quantitative analysis of SO₂ was investigated.

The boiling point of SO₂ is -10 °C, while that of SF₆ is -64°C, and there are 54 °C temperature difference between these two gases. Therefore, the temperature of secondary cold-trapping can be fixed at -10 °C with the injection volume of 50 mL. The temperature of primary cold-trapping is adjusted to -40 °C, -50 °C, -55 °C, -60 °C, and -65 °C, respectively. The standard gas selected ion spectra of 0.1 μL/L SO₂ is shown in Figure 1.

As can be seen from the Figure 1, the primary refrigeration temperature is lower than the boiling point of the component and higher than that of SF₆, the peak height of the SO₂ component increases slightly as the primary refrigeration temperature decreases.

To further verify this conclusion, the primary cooling refrigerating temperature was adjusted to -55 °C, -60 °C, and -65 °C while the other parameters were identical. The selected ion map of the 0.5 μL/L SO₂ standard gas was shown in Figure 2. It can be observed that the selective ion peak intensity of 0.5 μL/L SO₂ standard gas is dependent on the primary refrigeration temperatures, while those of the other components were almost independent.

3.3 Selection of secondary refrigeration temperature conditions
The primary refrigeration temperature was fixed at -55 °C, and the secondary refrigeration temperature was adjusted to be -40 °C, -30 °C, -20 °C, and -10 °C, respectively. The selected ion map of the 0.1 μL/L SO₂ standard gas was shown in Figure 3. It indicates that the peak intensity of SO₂ is increased with the increasing of the secondary cooling temperature. Therefore, the secondary cooling temperature as high as possible should be selected based on the boiling points of the contents.

3.4 Analyzed conditions for the concentrated samples
Table 1 shows the boiling point of the SO₂, H₂S, SO₂F₂ and SOF₂ components in SF₆. According to the boiling point of the decomposition products, the selected three-step refrigeration concentration injection conditions can be divided as follows: 1) the gas sample is subjected to the first-stage refrigeration. The first-stage cooling condition is that the cooling trap temperature of the M1 module is -61 °C. So that the SF₆ can be trapped in the M1 module, while the uncooled products flowed to the
M2 module; 2) The SF₆ decomposed products are further concentrated through the second-stage refrigeration. For the second-stage cooling condition, the temperature for cooling and adsorption is -10 °C, and the temperature for desorption is 220 °C. 3) The gas sample is subjected to the third-stage refrigeration. For the third-stage cooling condition, the M3 module cold focusing heating temperature is increased from -150 °C to 80 °C to volatilize the sample to the gas phase. The sample was injected by chromatography and mass spectrometry. The injection volume of the gas sample was 50 mL, and the injection rate was 1 mL/s with the sample transfer line temperature of 100 °C.

![Figure 3 Select ion map of 0.1 μL/L sulfur dioxide standard gas at different secondary cooling temperatures.](image)

| Decomposition products | Boiling point (°C) |
|------------------------|--------------------|
| SF₆                    | -64                |
| SO₂                    | -10                |
| SO₂F₂                  | -43.8              |
| SO₃F₂                  | -55.2              |
| H₂S                    | -60.4              |

3.5 Determination of the peak sequence of SF₆ decomposition products
The conditions for injection of the fixed concentrated samples device was to inject the four standard gases of SO₂, H₂S, SO₂F₂, and SO₂F₂. The full-scan mode was used to determine the peak sequence of the four components. The results in Fig. 4 show that the order of the peaks of the four components are SO₂F₂, SO₂F₂, H₂S, and SO₂, respectively. The time span for the peak of SF₆ was 4.0-4.6 min, which can be separated from the others clearly.

3.6 The Quantitative Analysis of SF₆ Decomposed Components
The selective ion monitoring was used to monitor selected specific ions and was used for quantitative analysis in GC-MS. Therefore, the quantitative analysis was performed using the selective ion scanning method. According to the standard mass spectra of the 4 components in the international standard mass spectrum, the characteristic ion fragment peaks of the 4 components were selected for quantitative scanning, and the selection of the ion scan conditions were set as follow: (1) solvent delay: 4.70 min; (2) select ion scan (SIM) parameters are shown in Table 2; (3) for the mass spectrometry (MS) area, the ion source is 230 °C and the quadrupole rod is 150 °C.
Figure 4 Peak sequence of SO$_2$, H$_2$S, SO$_2$F$_2$ and SOF$_2$ decomposition products of SF$_6$ four decomposition products.

Table 2. Select ion scan (SIM) parameters.

| Number | Testing components | Start time (min) | Detecting ions     |
|--------|--------------------|------------------|--------------------|
| 1      | SO$_2$F$_2$        | 4.70             | 67.00, 83.00, 102.00 |
| 2      | SOF$_2$            | 5.35             | 48.00, 67.00, 86.00 |
| 3      | H$_2$S             | 5.80             | 33.00, 34.00       |
| 4      | SO$_2$             | 6.50             | 48.00, 64.00       |

3.7 *The Comparison between the concentrated injection method and ordinary valve injection effect*

The concentration of 1 μL/L SO$_2$ gas was detected using the concentrated sampling method and the ordinary valve injection. As can be seen from Figure 5, the concentrated injection method is more sensitive to 1 μL/L SO$_2$, and the peak intensity of the component is 20 times larger compared with that obtained by the ordinary injection method. We can conclude that the detection limit is much lower. The concentrated injection method can significantly improve the detection sensitivity of SF$_6$ decomposition products.

Figure 5. Chromatogram of 1μL/L SO$_2$ gas obtained by the concentrated injection method and the ordinary injection method.
4. Conclusions
This work proposed a concentrated injection method based on the study of the SO₂, H₂S, SO₂F₂ and SOF₂ in sulfur hexafluoride (SF₆) combined with GC-MS. We improved the detection and basis of the gas released from the breakdown of SF₆ electronic equipment. The sensitivity for detection of 1 μL / L SO₂ can be highly enhanced with a much lower detection limit by the concentrated injection method. The intensity of the peak is increased by 20 times compared with that obtained by the ordinary injection method. It can be concluded that the method proposed in this study can improve the safety of the grid effectively with the reliable pre-warning system based on the advanced analysis method.

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