IOP Conf. Series: Materials Science and Engineering **274** (2017) 012038 doi:10.1088/1757-899X/274/1/012038

Research on technology of online gas chromatograph for SF6 decomposition products

L Li, X P Fan, Y Y Zhou, N Tang, Z L Zou, M Z Liu, G J Huang

Electric Power Research Institute of Guangdong Power Grid Limited Liability Corporation, Guangzhou, Guangdong, 510082, China

Abstract. Sulfur hexafluoride (SF6) decomposition products were qualitatively and quantitatively analyzed by several gas chromatographs in the laboratory. Test conditions and methods were selected and optimized to minimize and eliminate the SF6' influences on detection of other trace components. The effective separation and detection of selected characteristic gases were achieved. And by comparison among different types of gas chromatograph, it was found that GPTR-S101 can effectively separate and detect SF6 decomposition products and has best the best detection limit and sensitivity. On the basis of GPTR-S101, online gas chromatograph for SF6decomposition products (GPTR-S201) was developed. It lays the foundation for further online monitoring and diagnosis of SF6.

1. Introduction

With the rapid development of the power industry, a growing number ofsulfur hexafluoride (SF_6) electrical apparatuses were put into operation [1]. It is very important to keep track of the operation conditions of SF_6 electrical apparatus for the stability of the power [2]. Pure SF_6 gas is an ideal insulating medium, but it is easy to ionize and decompose under the conditions of high voltage discharge, arc and high temperature [3-4]. The decomposed products react with moisture and insulating materials in the equipment, and products such as sulfur tetrafluoride (CF_4), carbon disulphide (CS_2), sulfuryl fluoride (SO_2F_2), thionyl fluoride (SOF_2), sulfur dioxide (SO_2), Hydrogen sulfide (H_2S) and so on could also be generated [5-6]. Researches show that the formation of SF_6decomposition products is a symptom of an internal malfunction of the equipment [7-8]. The content, production rate and ratio of SF_6decomposition products are different in different conditions [9]. The failure cause, discharge level, development status and danger degree of the electric equipment can be judged by detecting the components of the SF_6decomposition products [10].

At present, the detection methods of SF_6 decomposition products are mainly electrochemical sensors, gas detection tubes, gas chromatography and so on [11-12]. Gas chromatography with high sensitivity and accurate quantification is the most frequently used method in the detection of SF_6 decomposition products at home and abroad [13]. However, commonly used chromatographs can only detect and analyse few kinds of SF_6decomposition products, and comprehensive detection of characteristic components of SF_6decomposition products cannot be achieved. In order to compensate for the lack of the existing technology, it is necessary to produce a set of chromatographic analytical instruments suitable for the detection of SF_6 electrical apparatus.

2. Methods and materials

2.1. Gas chromatograph

Serval kinds of gas chromatographs used in this study for comparison experiment were listed in Table 1.

Table 1. Gas chromatographs for comparison experiment

No.	Equipment type	Detector	Chromatographic column
1	Keysight, 7890	FPD + TCD	Gas Precapillary column
2	Aihua, GC-9560	PDD+PDD	PQ, Gaspro, GDX-1column
3	Shimadzu, GC2014C	FID+TCD	Porapak Q packed column
4	Keysight, 7890B	SCD+TCD	Gas Procapillary column
5	Guangdong Electric Power Research Institute, GPTR-S101	PDD	Polymer porous microsphere, Styrene two benzene polymer

2.2. Standard gas

Mixed standard gases from Dalian Special Gases Co., Ltd. are shown in Table 2. The 6 sets of standard gas (14 gases) were packed with 8L aluminum alloy seamless gas cylinders, and helium was used as the balance gas.

Table 2. Compositions and Concentrations of 14 Standard Gases

No.	Component	Concentration 10^{-6}(v/v)	No.	Component	Concentration 10^{-6} (v/v)
1	SO_2F_2	30	2	CF_4	30
	He	Balance gas		Air	30
3	SO_2	30		H_2S	30
	CO_2	30		COS	30
	He	Balance gas		He	Balance gas
4	C_2F_6	50	6	CS_2	30
	C_3F_8	50		CO	30
	He	Balance gas		H_2	30
5	SOF_2	30		He	Balance gas
	He	Balance gas		SF_6	5000

2.3. Gas sample compounder

Gas sample compounderis used for mixing two or more than two gases in a certain proportion and outputting gas with certain concentration. The gas sample compounder selected in this study wasRCS2000A type multi component dynamic gas sample compounder Beijing produced by Kingsun electronics Co., ltd. The principle of the compounder is based on the mass flow mixing method. The flow of dilute gas and species gases are controlled by a high precision mass flow controller. The dilute gas can be high purity nitrogen, helium and purified air. The species gases can be pure gas or mixed gas with certain concentration. A variety of standard gases from 10^{-8} to 10^{-2} can be disposed under accurate setting.

The main technical specifications of the gas sample compounder are as follows: (1) Conventional dilution rate is 1000:1, which is controlled by five-way MFC flow. (2) Flow repeatability is no higher than 0.3%. (3) Flow linearity error is no higher than ±0.5%. (4) Preheating time is 10 min. (5) Ambient temperature is range from 5℃ to 45℃. (6) Instrument power is 220VAC.

2.4. Analysis methods

2.4.1. Qualitative analysis of SF6 decomposition products. With the help of standard gases, to qualitatively analyze components and special compounds of SF_6 decomposition products by use of different detectors and chromatographic column. And then analyze and compare the separation efficiency.

2.4.2. Quantitative analysis of SF6decomposition products. With the help of standard gases, to quantitatively analyze components and special compounds of SF6 electric device gases by use of different detectors and chromatographic column. Analyze and compare the sensitivity, detection limit and other factors of the detector to determine the optimum detection method.

2.5. Online gas chromatograph

2.5.1. Apparatus structure. The online gas chromatograph (GPTR-S201) were developed by Guangdong Electric Power Research Institute, whichis used exclusively for online detecting of insulating gas decomposition products in SF_6 electrical apparatus. It is composed of sampling system, chromatographic column, temperature control system and detector. The sampling system consists of three 6-way valves, a quantitative sampling tubes, a 3-way valve and a piping system. The chromatographic column is the core component of the online gas chromatograph, and mainly consists of two chromatographic columns, located in temperature programming box. The chromatographic column 1 is a 1/8 packed column (5m, and the filler is styrene two benzene polymer), which can effectively separate SO_2F, SO_2F_2, CF_4, H_2S, C_2F_6, CS_2 and C_3F_8 in the condition of SF_6 background gas. The chromatographic column 2 is 1/8 packed column (5m, and the filler is a polymer porous microsphere), which can effectively separate SO_2, COS and other components under the SF_6 background gas. The temperature of the temperature control box is range from normal temperature to 350℃. The temperature control system is mainly composed of chromatographic column box, heating rod and platinum thermal resistor. The chromatographic column box is a carrier that incorporates all the components of the temperature control system, and commonly its volume is too large (200mm*300mm*400mm). In this study, a small portable chromatographic column (100mm*100mm*100mm) has been developed, which is easy to use and replace. The detector of the online gas chromatograph is a helium ion pulse detector. Compared with other detectors, the helium ion pulse detector has the advantages that the detection sensitivity is high, and the minimum concentration detection in the gas reaches 5ppb grade. The experiment proves that the PPM grade gas sample can be detected as long as 0.5 ml standard sample gas is sampled. Butit is necessary to use high purity helium as carrier gas (high purity helium is helium with purity above 99.999%), and keep high temperature aging at 120℃ to ensure the peak velocity.

2.5.2. Experimental method. The analysis process of the online gas chromatograph for SF6 decomposition products includes initialization, gas sampling, gas analysis, and gas switching. The debugging and testing of GPTR-S201 chromatograph mainly include qualitative analysis of each component of SF_6 decomposition products. The definite means are as follows: with the help of standard gases, use online gas chromatograph (GPTR-S201) to analyze components of SF_6 decomposition products. And make a comparison with gas chromatography mass spectrometry (GC-MS) existed in the laboratory to determine the qualitative analysis result of GPTR-S201. Standard gas and gas sample compounder are the same as above.

2.5.3. Analysis condition. The analysis conditions of GPTR-S201 gas chromatograph are: Column temperature: 60℃. Detector temperature: 150℃. Carrier gas (high purity helium: purity 99.99%):0.4 MPa. Injection rate: 50 mL/min. Injection pressure: atmospheric pressure.

3. Results and discussion

3.1. Comparison results of each gas chromatograph

The qualitative and quantitative results of each detection method are shown in table 3. By studying and comparing different gas chromatograph, and carrying on the real sample testing, the qualitative and quantitative characteristics of SF_6decomposition products were investigated. It was found that about 9 kinds of SF_6decomposition products including SO_2, H_2S, SO_2F_2, SOF_2, CS_2, COS, C_3F_8, C_2F_6, CF_4 and so on can be can be completely separated and detected by GPTR-S101 and Huaai GC9560.Agilent 7890 and Agilent 7890B are mainly used for qualitative and quantitative analysis of sulfur-containing substances, and Shimadzu GC-2014 is mainly used for the detection of carbon containing substances. So, three conclusions can be drawn as follow: (1) For all decomposition products under the SF_6 background gas, the PDD detector showed good response performance, and the minimum detection limit reached 0.01ppm. (2) In order to effectively separate decomposition products (SO_2, H_2S, SO_2F_2, SOF_2, CS_2, COS, C_3F_8, C_2F_6, CF_4 and so on) in background SF6, Huaai GC9560 was designed to combine GAS pro, PQ and GDX-1 column and a plurality of capillary column with PDD detector together. It leads to complicated equipment, difficult operation, and high cost of equipment, which is not conducive to the promotion and application of the instrument. (3) GPTR-S101developed by Guangdong Electric Power Research Institute can effectively separate and detect SF6 decomposition products. Compared with other detection method, GPTR-S101 has best the detection limit and sensitivity. In addition, GPTR-S101 has a PDD detector and two packed columns. It can work without ignition, which greatly simplify the operation of the instrument. Its packed column greatly simplifies the structure of the instrument, which is conducive to the development of portable and online SF6 chromatograph.

Table 3. Comparison of detection methods established by various gas chromatographs

Type	Detectable component	Detection limit (ppm)	Sensitivity (mV/ppm)	Quantitative repeatability (%)
Keysight, 7890	SO_2, CF_4, SO_2F_2, C_3F_8, C_2F_6	0.5-5	0.22-1.98	1.3-4.2
Aihua, GC-9560	SO_2, H_2S, SO_2F_2, SOF_2, CS_2, COS, C_3F_8, C_2F_6, CF_4	0.03-0.6	0.97-5.33	0.4-2.5
Shimadzu, GC2014C	CF_4, C_3F_8, C_2F_6	1.7-5.4	0.34-2.36	2.3-6.3
Keysight, 7890B	COS, H_2S, SO_2F_2, CS_2, SO_2	0.2-1.8	0.5-4.3	1.1-5.4
Guangdong Electric Power Research Institute, GPTR-S101	SO_2, H_2S, SO_2F_2, SOF_2, CS_2, COS, C_3F_8, C_2F_6, CF_4	0.01-0.6	4.88-13.42	0.3-2.2

3.2. Online gas chromatograph

Using analysis method above, the 14 kinds of standard gases in Table 2 are analysed separately and corresponding spectrums are shown in the following Figures.1-5. As can be seen from the spectrums, 14 kinds of standard gases including H_2, CO, CF_4, COS, H_2S, CO_4, SF_6, SO_2F_2, SOF_2, COS, C_2F_6, C_3F_8, CO_2 and SO_2can be effectively separated and detected.

By the analysis of 14 standard gases, the retention time of each gas component is shown in table 4. Table 4 shows that 14 gases can be well separated, and the minimum separation coefficient is 1.66, which means that all components can be separated effectively. After investigation, it is found that there are no similar products on the market at present.

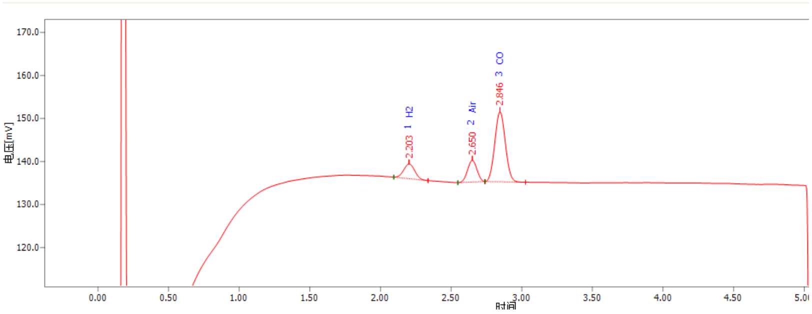

Figure 1. H2, Air and Spectra

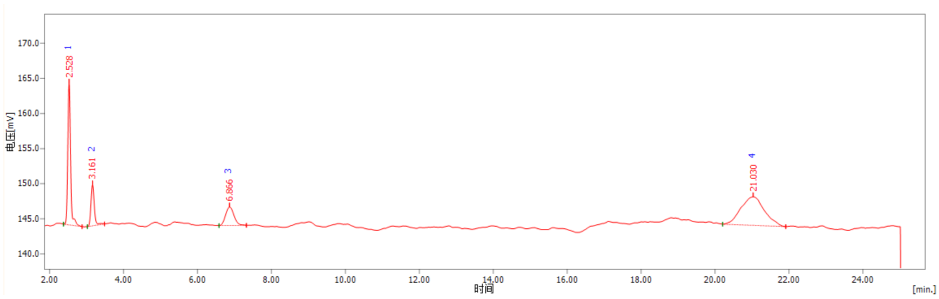

Figure 2. Air, CF4, COS and H2S spectra

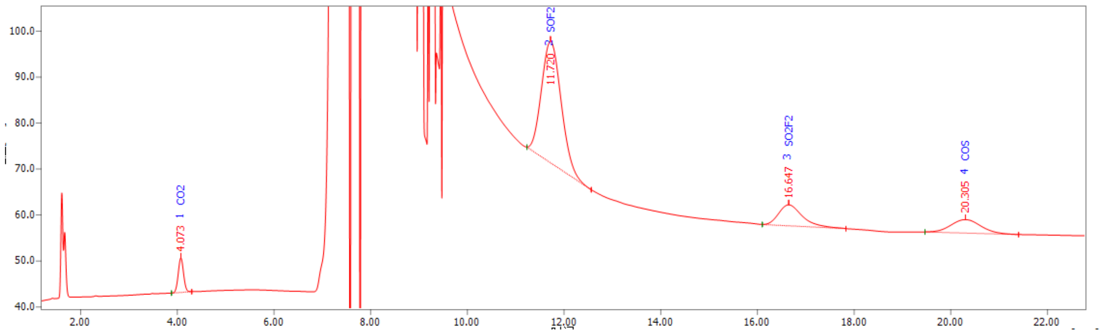

Figure 3. Air, CO4, SF6, SO2F2, SOF2 and COS spectra

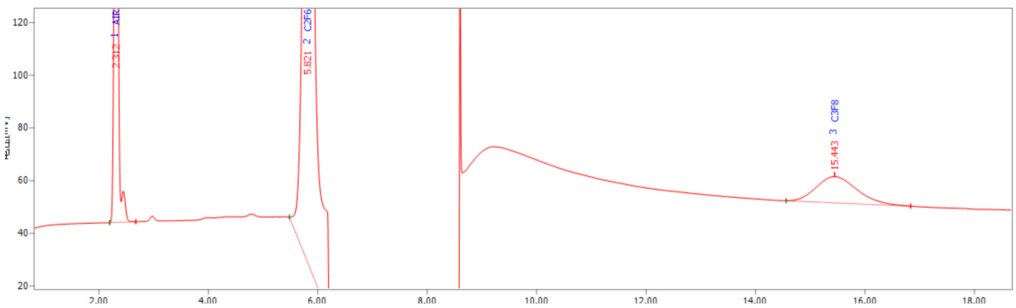

Figure 4. Air, C2F6and C3F8 spectra

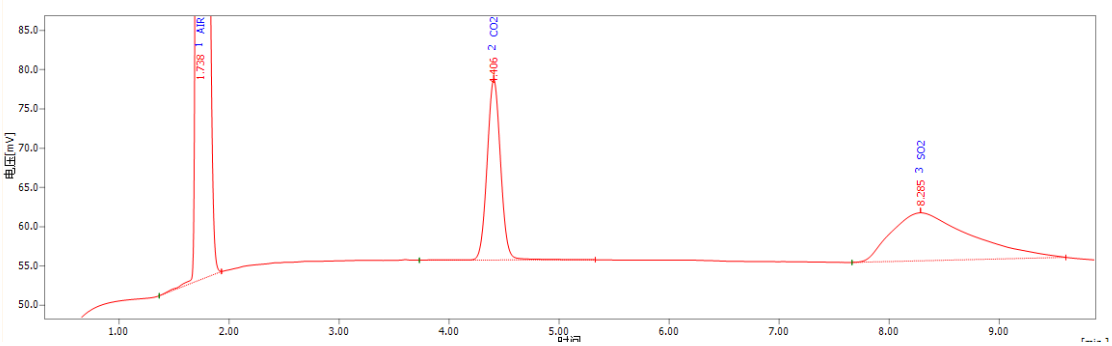

Figure 5. Air, CO2 and SO2 spectra

Table 4. Retention time of components of gases

No.	Component	Retention time (min)
1	H_2	2.203
2	Air	2.650
3	CO	2.846
4	CF_4	3.567
5	CO_2	5.467
6	SO_2	7.085
7	C_2F_6	9.490
8	SF_6	11.234
9	SO_2F_2	14.862
10	C_3F_8	17.657
11	SOF_2	15.608
12	COS	19.866
13	H_2S	21.071
14	CS_2	33.768

4. Conclusion

SF6 decomposition products were analysed and compared by using different methodsin the laboratory. The study found that GPTR-S101 developed by Guangdong Electric Power Research Institute can separate and detect 9 kinds of SF6 decomposition products including SO_2, H_2S, SO_2F_2, SOF_2, CS_2, COS, C_3F_8, C_2F_6, CF_4 and so on. It has the advantages of simple structure, high sensitivity and low detection limit. Online gas chromatograph GPTR-S201 for SF_6decomposition products was developed on the basis of GPTR-S101. 14 kinds of SF_6 decomposition products can be detected by GPTR-S201. The detection limits are ppm. There is no similar instrument on the market at present.

Acknowledgments

This study was financially supported by the Technology Project of China Southern Power Grid (GDKJQQ20152042).

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