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Short Review

Mechanism of Formation of SF_6 Decomposition Gas Products and its Identification by GC-MS and Electrochemical methods: A mini Review

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The SF_6 is commonly used as an insulating gas in different applications; however the SF_6 can be easily exploded into different decomposition gas products when subjected to electrical discharge, such as electric arc, spark or corona. The resulting decomposition gas products are more toxic, corrosive and harmful to human beings and the environment. Till date, lots of attentions have been paid to monitor the SF_6 decomposition products; since the properties of SF_6 decomposition products are completely different from pure SF_6. The different methods for sensing the SF_6 decomposition products in the past few decades and the possible mechanism of decomposition of SF_6 into gaseous products by different discharge methods at the insulator surface are addressed in this review. In addition, two of the important methods, such as gas chromatography–mass spectrometry (GC-MS) and electrochemical method, were highlights and discussed for the detection of SF_6 decomposition products.

Keywords: SF_6 decomposition products; discharge methods; GC-MS, electrochemical methods; SO_2

1. INTRODUCTION

Sulfur hexafluoride (SF_6) is a colorless, orderless, non-toxic, non-flammable gas and widely known for the applications in gas-insulated switchgear (GIS), gas-insulated transmission lines (GITL), electrostatic accelerators, X-ray equipment and pulse power apparatus [1–5]. With the prosperities of good dielectric and heat transfer and the ability to regenerate after arc interruption, SF_6 have been applied for both arc interruption and insulation of circuit breakers [6]. Although SF_6 is highly stable molecule at normal operating temperatures, a portion of SF_6 molecules would be decomposed to complicated gas and solid byproducts by reacting with little water, electrode and solid insulated material under electrical stress conditions caused by arc, spark, and partial discharge [7]. The decomposition products and the mechanism of SF_6 have been extensively studied, the gas byproducts include SOF_2, SO_2F_2, SOF_4, S_2F_{10}, SO_2, HF, and solid byproducts include aluminum fluoride, tungsten fluoride, and so on [8–11]. Analyzing SF_6 decomposition products has the potential to be a powerful diagnosis method for partial discharge detection [12]. Mostly, the molecular sieves containing activated alumina is provide in each pole tank and this molecular sieve absorbed the decomposition gases and eliminates most of these gaseous decomposition products.

Figure 1. The SF6 reactor tank (A), closed (B) and opened pole tank (C) with molecular sieves and lit of the pole tank (D).

The optical image of insulator surface containg molecular sieves after the operating the pole tank is shown in Fig. 1. The SF6 reaction tank, the closed reaction pole tank with molecular sieves, the opened pole tank with molecular sieves, and the lit of the pole tank with molecular sieves after the SF_6 decomposition are represented in (A), (B), (C), and (D), respectively. The SF_6 decomposition adsorbed molecular sieves are further used for the detection of decomposition products using the chromatographic or other methods.

According to health and safety point of view, the toxicity of SF_6 decomposition products must be identified in order to check the equipment. Previously, SF_6 decomposition products have been detected by various methods, such as a gas chromatography [13], a gas chromatography/mass spectrometry [14], an ion-conductive solid eletrolyte [15], and Fourier transformation infrared (FTIR) spectroscopy [16] mainly in the gas state of SF_6. In order to detect the decomposition products, the possible decomposition mechanisms, decomposition rates, properties of the decomposition products and the interaction of the by-products with the equipment are required [17]. Hence, this review focuses on the major investigations and the possible mechanism of SF_6 decomposition gas products formation which have reported in the literature.

2. MECHANISM OF FORMATION OF SF_6 DECOMPOSITION PRODUCTS

The SF_6 is mostly decomposed by electrical gas discharge (spark and corona conditions) and react with water and oxygen to form the different decomposition gas products from the fundamental gas-phase chemical processes [18]. The different decomposition gases products are formed under explore the decomposition SF_6 in different conditions. On the basis of the previous literature reports, the majority of decomposition products of SF_6 were lower fluorides of sulfur compounds [19–29]. First, the thermal dissociation of SF_6 to SF_4 takes place at arc temperatures; the SF_4 further reacts with other molecules to form variety of compounds. The well known methods for the electrical discharge of SF_6 are arc, spark and corona discharge methods [20]. The formation of SF_6 decomposition and the reaction of decomposition products with water and oxygen are shown in Fig. 2. It can be seen that the major products of the decomposition reaction are sulphur oxides, while others are fluoride compounds. The concentrations of decomposition products are directly dependent on spark conditions and energy.

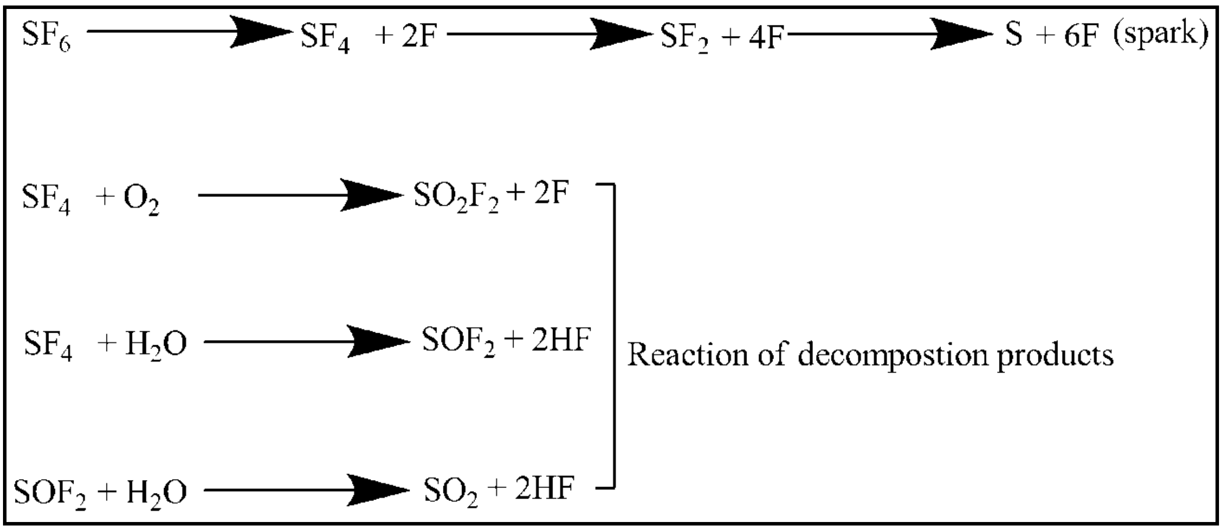


Figure 2. The formation of SF_6 decomposition and the reaction of decomposition products with water and oxygen.

3. DETECTION OF SF_6 DECOMPOSITION PRODUCTS

So far, different methods have been developed for the detection of SF_6 decomposition products, such as gas chromatography, ion mobility spectrometer and FTIR spectroscopy. Some of the previously reports of detection methods and electrode surface for the decomposition products are shown in Table 1.

Table 1. Identification of SF_6 decomposition products by different electrodes and methods.

Decomposition products	Electrode	Detection method	Ref.
SO_2, SOF_2	Cu–Au	IR	19
SiF_4, SOF_2, S_2F_2, CuF_2	Cu	MS	20
SO_2, SF_2, SO_2F_4	Al	GC-MS	21
SOF_2, SO_2F_4, CuF_2	Cu	GC-MS	22
SF_4, SOF_2, $S0F_4$, SO_2F_2, SiF_4, SO_2, WF_6	W	MS	23
SF_4, SOF_2, SO_2F_2, SOF_4, S_2F_{10}, S_2F	-	GC	24
SF_4, SOF_2, SOF_4, SO_2F_2, S_2F_{10}, S_2F	Cu	GC	25
SOF_2, SOF_2, SOF_4, S_2F_{10}, $S_2F_{10}O$	Al	GC	26
Phenol	ASPCE	DPV	27
SO_2	SPCE	DPV	28
SO_2F_2, SOF_2, SO_2	Au-Doped TiO_2	GC	29
SOF_2			30

It can be concluded from the table that the most of the decomposition compounds are sulphur oxides and fluorides. The GC-MS and GC were commonly used for the detection of the decomposition products [21–30]; recently we included the electrochemical method for the detection of SO_2 [27, 28]. The scheme for formation of SO_2 and its electrochemical detection is shown in Fig. 3.

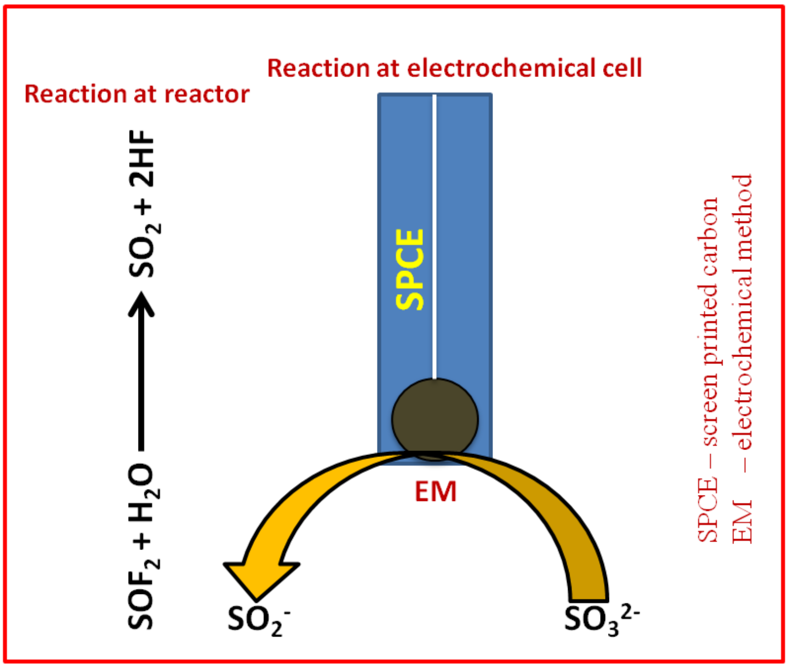


Figure 3. The scheme for formation of SO_2 and its electrochemical detection by electrochemical method.

The SO_2 first extracted into the suitable electrolyte solution and detected by electrochemical method using the modified electrodes. In our earlier study, we have used screen printed carbon for the detection of SO_2 [27]. First the SO_2 adsorbed on the electrode surface and reduced to SO_3^{2-} by voltammetric methods [31]. The possible mechanism for the reduction of SO_2 in different pH solutions are shown in at Fig. 4.

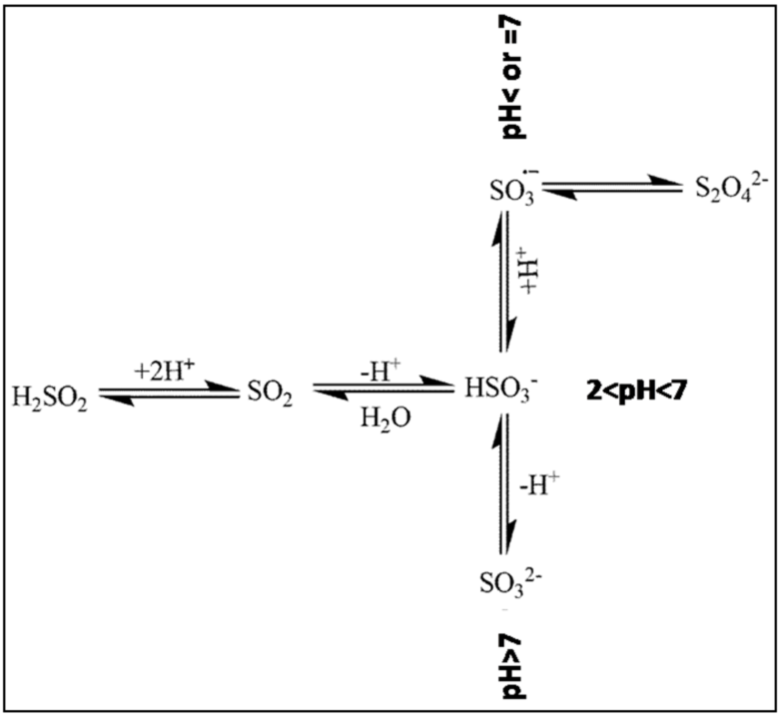
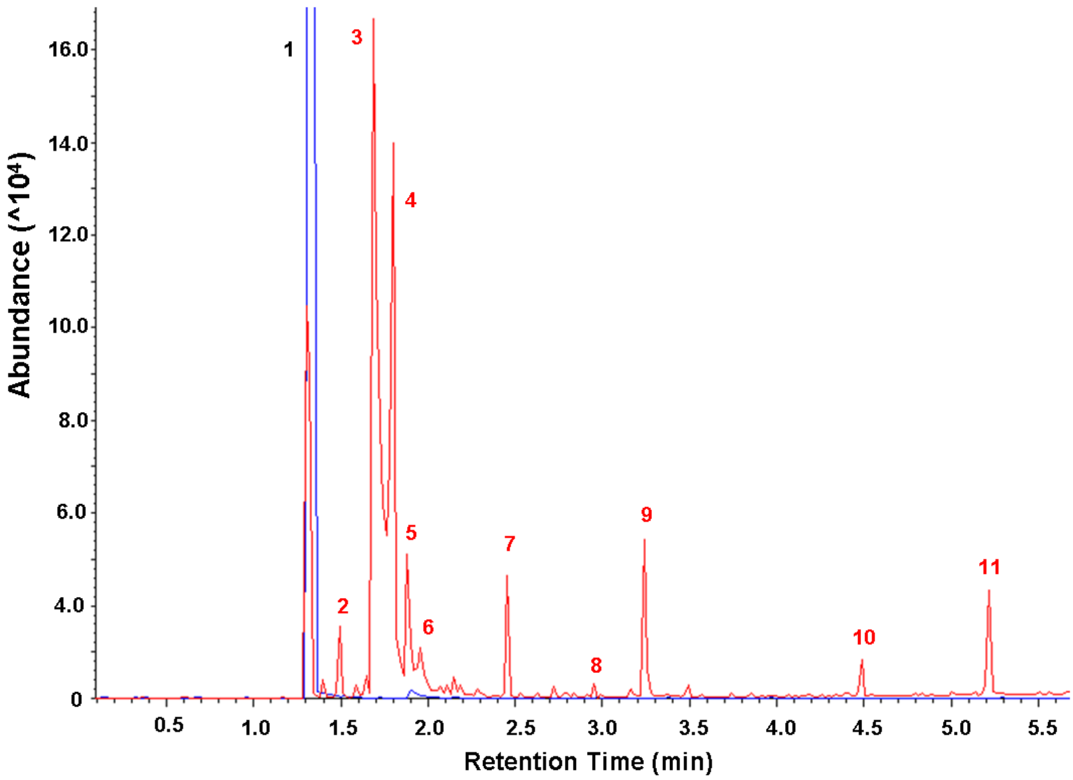


Figure 4. Electrochemical reduction mechanism of SO_2 in different pH solutions.

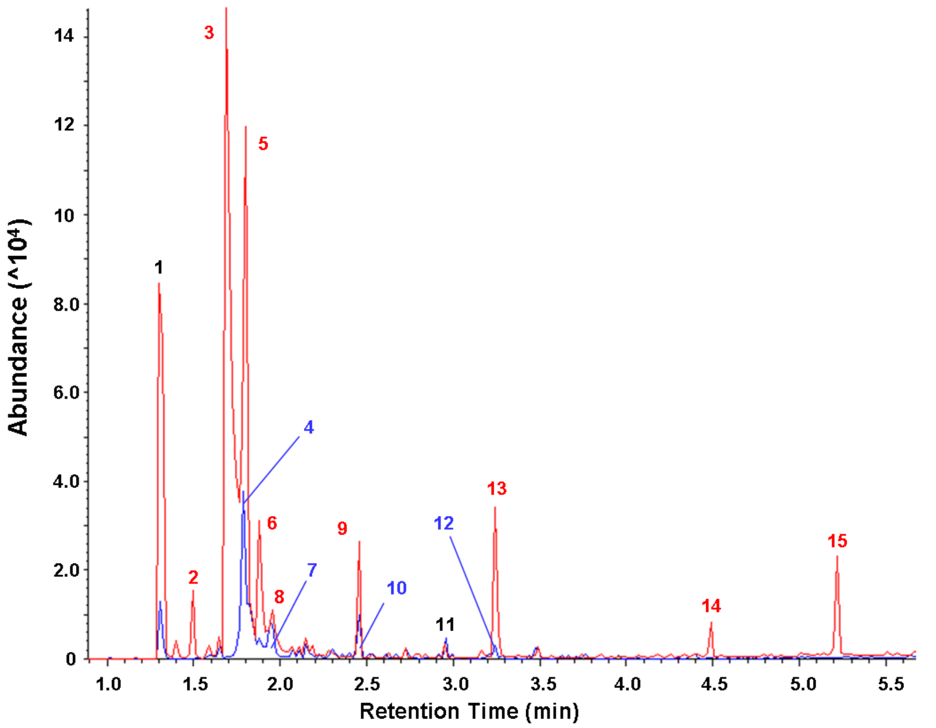
We also provided the analysis of the solvent extracted SF_6 decomposition products by using the GC-MS. The total ion chromatography (TIC) of GC-MS for SF_6 decomposition products by injecting between the gas sample and the methanol extracted sample were compared and shown the color blue and color red in Fig. 5, respectively.



No.	RT (min)	MW	Formula	Compound Candidate
1	1.30	146.0	SF_6	Sulfur hexafluoride
2	1.50	75.9	CS_2	Carbon disulfide
3	1.69	64.0	SO_2	Sulfur dioxide
4	1.80	140.1	C_8H_9FO / $C_8H_{12}S$	2-Fluorobenzyl alcohol, methyl ether / Thiophene, 3,4-diethyl-
5	1.88	111.0	CH_5NO_3S	Aminomethanesulfonic acid
6	1.96	64.0	$C_2H_2F_2$	1,1-Difluoroethene
7	2.45	122.1	$C_8H_{10}O$	Phenylethyl Alcohol
8	2.96	106.1	C_8H_{10}	p-Xylene
9	3.25	110.0	$C_2H_6O_3S$	Dimethyl sulfite
10	4.49	101.1	$C_2H_3N_3S$	Aminothiadiazole
11	5.22	138.1	$C_8H_{10}O_2$	Tyrosol / 2,5-Dimethyl-1,3-benzenediol

Figure 5. The SF6 decomposition products gas injected (blue line) and purged in MeOH (red line) sample analysis by GC-MS. Total ion chromatography (TIC) and candidate compound list table. Numbers in red represent only exist in the sample purging in MeOH, and numbers in black is in both samples.

At least 10 more SF_6 decomposition compounds were observed in the TIC of the GC-MS analysis by injecting the solution extracted from the gas sample than by injecting the gas sample alone. By matching the mass spectrum with database of the NIST14 library, 11 organic compounds were identified and represent in the table below. Peak 1 is SF_6 shown in both TICs. Peaks 2, 3, 4, 5, 9, and 10 are identified as carbon disulfide (CS_2), sulfur dioxide (SO_2), thiophene,3,4-diethyl-($C_8H_{12}S$), aminomethanesulfonic acid (CH_5NO_3S), dimethyl sulfite ($C_2H_6O_3S$), and aminothiadiazole ($C_2H_3N_3S$), respectively.



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3	1.69	64.0	SO_2	Sulfur dioxide
4	1.79	104.1	$C_4H_{12}OSi$	Trimethylsilylmethanol
5	1.80	140.1	C_8H_9FO / $C_8H_{12}S$	2-Fluorobenzyl alcohol, methyl ether / Thiophene, 3,4-diethyl-
6	1.88	111.0	CH_5NO_3S	Aminomethanesulfonic acid
7	1.94	118.1	$C_6H_{14}O_2$	2,2-Dimethoxybutane
8	1.96	64.0	$C_2H_2F_2$	1,1-Difluoroethene
9	2.45	122.1	$C_8H_{10}O$	Phenylethyl Alcohol
10	2.46	92.1	C_7H_8	Toluene
11	2.96	106.1	C_8H_{10}	p-Xylene
12	3.24	106.0	$C_3H_6O_2S$	2-Mercaptopropanoic acid
13	3.25	110.0	$C_2H_6O_3S$	Dimethyl sulfite
14	4.49	101.1	$C_2H_3N_3S$	Aminothiadiazole
15	5.22	138.1	$C_8H_{10}O_2$	Tyrosol / 2,5-Dimethyl-1,3-benzenediol

Figure 6. The SF_6 pure gas (blue line) and decomposition gas (red line) purged into MeOH analysis by GC-MS. Total ion chromatography (TIC) and candidate compound list table. Numbers in blue represent the compounds only exist in pure gas, in red are only exist in decomposition gas, and in black are in both samples.

The TICs of pure SF_6 and SF_6 decomposition products in methanol solvent were compared and shown in color blue and color red of Fig. 6, respectively. According to the candidate compounds list table below, the compounds identified in SF_6 decomposition products shown in red color of Fig. 6 are not found in pure SF_6 sample shown in blue color of Fig. 6. Therefore it has been confirmed that all are produced after SF_6 decomposition. Among these 6 sulfide trace compounds found in the methanol extraction of SF_6 decomposition products, carbon disulfide (CS_2) could be a good candidate target compound to develop the diagnosis method for the degradation of SF_6 since the peak 2 is well separated and no interfered with other compounds from the pure SF_6 or its other decomposition compounds.

The possible generation of CS_2 is suggested as equation (1), mainly due to the reaction between the discharged ionization, like SF_x or H_2S [32], and the carbon from solid organic insulator.

$$SF_6 \longrightarrow S(g) + C(s) \longleftarrow \text{organic} \qquad (1)$$

$$S(g) + C(s) \longrightarrow CS_2(g)$$

$$\Delta H = -11.6\ \text{KJ/mol}$$

4. CONCLUSIONS AND PROSPECTIVES

In summary, the above discussion clears that the SF_6 decomposition products were identified by different methods; GC and GC-MS techniques are frequently used for the detection of decomposition gases. Sulphur oxide and fluorides are the primary products of SF_6 decomposition products; though other compounds are in trace amount. The trace amount of SF_6 decomposition products after methanol extraction become detectable by GC-MS and the well separated TIC has provided that the more than ten decomposition products were produced. According recent advances in electrochemical methods for sensing of gas molecules and hazardous chemicals, we have showed the detection of SO_2 and phenol using the SPCE and activated SPCE. As future perspectives, this review gives the possible idea for the electrochemical sensing of sulphur oxides using the different modified electrodes in the near future.

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