

Research Article



Importance of Calibrating Analytical Equipment for Detecting and Quantifying Degradation Byproducts of C4F7N/CO2/O2 Gas Mixtures Insulation Fluid

Muhammad Bilal Arif^{1,2}, Christophe Coquelet¹, Maxime Lacuve^{2*}, Frank Jacquier², Rachel Calvet¹

Abstract

In the past few years, the C4F₇N/CO₂/O₂ gaseous blend has been recognized as the best promising alternatives to SF, gas, allowing to keep the minimum dimensional and environmental footprint of high voltage power transmission equipment's versus other alternatives. In the event of extreme thermoelectric stress, similar to SF₆ the gas mixture undergoes dissociation and produces a diverse range of byproducts in various concentrations. Analytical technologies such as gas chromatography coupled to mass spectrometry (GC-MS) and Fourier Transform Infrared (FTIR) are the key devices that can have the accurate estimation of qualitative and quantitative measurements of byproduct gas samples. Analysis of the arced gas sample reveals a range of byproducts, including CO, CF₄, C₂F₆, C₃F₈, C₂F₄, C₃F₆, COF₂, CF₃CN, C₂F₆CN, CF₂=CF-CN, (CN)₂, CF₃-N=CF₂, CF(CF₃)₂-CO-NH₂, and (CH₃)₂SiF, that can be found as trace-level. However, due to the limited availability of standard gas in the market, only five gases, CF_a, C₂F₆, C₃F₈, CF₃CN, and COF, were selected as standard for quantification. In our GC-MS method development, achieving complete peak separation was not possible due to the potential matrix effect of the sample. However, the peak area corresponding to the molecular ion of CF₄, C₂F₆, C₃F₈, CF₃CN, and COF, was carefully determined, and the regression curve was plotted for each molecule individually. In COF, results, the standard deviation was 69%, which led us to develop the FTIR methodology for COF, with the classical least squares (CLS) method, in which the standard deviation drops to 4% from 69%.

Keywords: C₄F₇N-CO₂-O₂ gaseous mixture; Gas Chromatography - Mass Spectrometry (GC-MS); byproducts.

Introduction

Sulfur hexafluoride (SF₆) is broadly used as the main insulating and interrupting medium in industrial circuit breakers due to its excellent arc quenching, dielectric, and insulating performance. However, SF₆ gas has the global warming potential (GWP) of 24,300 and a 1,000-year atmospheric lifetime, posing significant environmental threats [1]. Identifying a suitable SF₆ replacement for higher voltage devices was challenging; however, the insulating C₄F₇N-CO₂-O₂ gaseous blend proved as a suitable substitution. It preserved the compact footprint and performance of the SF₆ devices while considerably reducing its overall carbon footprint [2]. In the past few years, rigorous research has been conducted on the electric breakdown and thermal aging of the various ranges of composition of the C₄F₇N/CO₂/

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O, mixture, and various kinds of byproducts have been revealed by the GC-MS and FTIR technologies. Kieffel et al. [2] detected the CO, COF₂, C₃F₆, CF₃CN, and C₂F₅CN by-products in their thermal stability tests at 800 °C of the C₄F₇N/CO₂ gas mixture. Zhang and his co-workers [3] conducted the AC discharge breakdowns of C₄F₇N/ CO2, and numerous by-products, including CO, CO2, CF4, C₂F₄, C₂F₆, C₃F₈, C₄F₁₀, CF₃CN, C₂F₅CN, C₂F₃CN, C₂N₂, HCN, and HF, were detected by gas chromatography and mass spectrometry (GC-MS) technology. Substitution of buffer gases such as N₂ and air instead of CO₂ also causes the production of similar byproducts. Zhao et al. [4] revealed several byproducts, including CF₄, C₂F₆, C₃F₈, C_2F_4 , C_3F_6 , CO, CO_2 , $C_2O_3F_6$, $F_3CC = CCF_3$, $CF_3CF = CFCF_3$, (CF₃)₃CF, CF₃CN, C₂F₅CN, and (CN)₂, produced during corona discharge of (CF₃)₂CFCN/CO₂, (CF₃)₂CFCN/N₂, and (CF₂)₂CFCN/air mixtures. Ye et al. [5] conducted the 200 breaking tests of a gas mixture of 57% C₄F₇N in air. GC-MS technology reveals the byproducts, including CF₄, C_2F_6 , C_3F_8 , CF_3CN , $C_4F_{10}N_2$, CO_2 , and $(CN)_2$. Iddrissu et al., [6] performed the tests on a 20% C₄F₇N:80% CO₂ gas mixture using spark gaps under a pressure of 6.2 bar relative and collected a gas sample containing prominent byproducts, including CF₄, C₂F₆, CF₂=CF-CF₃, CF₃CN, and CF₂=CF-CN, after 1000 DC breakdowns. Additionally, fluorocarbons, including CF₄, C₂F₆, and C₃F₈, are common byproducts generated from the electric breakdown of potential insulation gases such as C₅F₁₀O [7] and C₆F₁₂O [8]. Gas Chromatography, coupled with Mass Spectrometry (GC-MS), is a crucial analytical method employed today to identify the diverse range of chemical species present in the given gas sample. Applications of GC-MS include environmental analysis, explosive investigation, drug evaluation, and the identification of unknown substances. GC utilizes a capillary column whose dimensions (length, internal diameter, and film thickness) and stationary phase depend on the type of molecules that need to be separated based on their chemical structure and boiling point without decomposition. Thermoelectric stress causes the decomposition of the gases into their corresponding byproducts. Thus, it is essential to establish an optimized GC-MS configuration for identifying and quantifying key byproducts produced under thermoelectric stress of gas mixture. Accurately distinguishing and quantifying these molecules is a crucial step toward determining their concentration range, ensuring both operator protection and device reliability. Additionally, FTIR technology is also employed to detect and quantify molecules, which may have chemical interactions with the stationary phase of the GC column (trifluoropropyl methylpolysiloxane).

Polluted gaseous sample by-products detection and quantifications

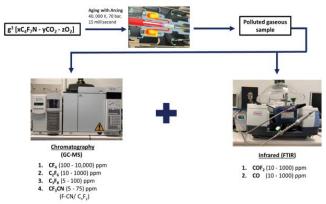


Figure 1: Explanation of the polluted gaseous sampling process after the electrical arcing event in a typical industrial circuit breaker (Copyright: GE Vernova property)

In this study, we developed GC-MS and FTIR methodologies to identify the byproducts that are present in contaminated gas samples retrieving from the thermoelectric stress of those gas mixture, enabling rapid and simultaneous quantification of a variety of the gas species ranging from the level of ppm to percentage.

Material and Methodology

Gas Chromatography – Mass Spectrometry (GC-MS) methodology

A quadrupole GC-MS Agilent Technologies 7890 A with triple-axis detector equipped with the Restek Rtx-200 GC column (length 105 m, inner diameter 0.25 mm, film thickness 1.00 µm) is utilized for the detection and calibration of gaseous mixtures, modified to minimize external contamination during measurements. The selected GC column with a trifluoropropyl methylpolysiloxane stationary phase enables discriminatory interactions with nitro, halogen, and carbonyl groups. Ultra-high-purity helium (99.9999 vol% by gas chromatography) was run in the device as the carrier gas, with a constant flow rate of 5 mL/min during sampling. For sample injection, a consistent flow rate of 1 mL/min was maintained using a flowmeter to ensure precise measurement. A dose of N₂ gas at 10 mL/min was run through the system for the duration of 10 minutes to purge the GC instrument before passing each sample. Two temperature ramps were set at a constant rate of 15 °C/min, reaching 100 °C and 180 °C, over a duration of 15.2 min and 22.1 min, respectively (Table 1). Scan mode with the range of 15 to 600 (2.51 scan s-1) is used in mass spectrometers with electron ionization (70 eV). Certified standards of CF₄ (100, 1000, 10,000) ppm, C₂F₆ (10, 100, 1000) ppm, C₃F₈ (5, 50, 100) ppm, COF, (10, 100, 1000) ppm, and CF₃CN (5, 25, and 75) ppm with CO₂ buffer gas were used to construct the regression curve for each gas individually. These three standards were supplied



by ABCR GmbH & Co KG. Additionally, the selective ion was m/z 69 for CF₄; m/z 119 for C₂F₆; m/z 169 for C₃F₈; m/z 76 for CF₃CN; and m/z 47 and 66 for COF₂. The total duration of 22 minutes gives sufficient period for the peak detection and separation of the compound. The peak areas on the chromatogram were used to establish the regression curve against known concentrations of CF₄, C₂F₆, C₃F₈, CF₃CN, and COF₂ gas mixtures.

Fourier Transform InfraRed (FTIR) methodology

Since, in the case of FTIR technology [10], only a defined volume cell filled with the gas sample is utilized to obtain the measurements. FTIR (Nicolet iS50 FTIR 2-meter gas cell) was employed to obtain an infrared spectrum of standard gas containing (10, 100, and 1000) ppm of COF₂, and the methodology to calibrate the COF₂ is present in Table 2. The window material is made from potassium bromide (KBr), with a light transmission band of 400-4000 cm⁻¹, which satisfies the experimental requirements.

Results and Discussion

Qualitative analysis

Figure 2 represents the total ion chromatogram (TIC) peak of all the chemical species CF₄, C₂F₆, C₃F₈, CF₃CN, COF₂, and CO, presented in a highly concentrated standard gas bottle, which can be identified with their unique m/z of fragments or molecular peaks. CF₄, C₂F₆, and C₃F₈ are separated with the current methodology; however, CF₂CN, CO₂, and COF₃ could not be distinguished. Normally, lowering the flow rate and sample dilution gives better separation of the peaks and avoids their overlapping; however, in our case, it was not possible to achieve a complete separation of all the peaks due to the matrix effect of all fluorocarbons. Since CO₂ is the background gas in the standard gas mixture, it is likely that fluorocarbon molecules such as CF₃CN and COF₂ co-migrate with the abundant CO, molecule in the capillary column and subsequently flow into the ionization chamber. This phenomenon causes the suppression of CF₃CN and COF₃ ions and makes the transfer difficult towards the detector [11]. In such an instance, we make sure the mass spectrum of each peak corresponds to the molecule (more information in supplementary data), and the optimum separation was observed at 3 mL/min flow rate (Table 1).

Quantitative analysis

Figures (3a, 3b, 3c, 3d, 3e, and 3f) represent the standard linear curves (regression curve) obtained at 60-days' time intervals for all the molecules in the standard gas sample. The linear equation is given by Equation 1, where S_{avg} denote the average peak area of a specific ion, c represents the concentration, a represents the slope (response factor, R_f), and b represent the intercept value.

Table 1: GC-MS Methodology Parameters

#	GC Parameters	Setting			
1	Temperature ramp rate 1	32 °C for 7 min (isotherm)			
2	Temperature ramp rate 2	15 °C/min up to 100 °C hold time 3.75; Run time = 15.283 min			
3	Temperature ramp rate 3	15 °C/min up to 180 °C hold for 1.5 min; total run time = 22.117 min			
4	Split ratio	50:1			
5	Injector inlet temperature	150			
6	Interface temperature	250			
7	Septum purge flow (mL/min)	3			
8	Injection flow rate (mL/min)	J			
9	Make up flow He (mL/min)	5			
10	Carrier gas	He			

Table 2: FTIR methodology

#	Parameters	Setting
1	Wavenumber range (cm ⁻¹)	500 - 4000
2	Gas pressure (mbar)	1000
3	Operating Temperature (°C)	40
4	Number of scans	16
5	Resolution	0.5
6	Detector	DTGS (KBr)*

^{*}Deuterated Triglycine Sulfate (DTGS) detector

$$c = aS_{ava} + b \tag{1}$$

Apparently, CF₄, C₂F₆, C₃F₈, and CF₃CN curves are slightly moved toward y-axis after two months and can be attributed to the GC column aging. Since, the presence of the gases, such as CO₂ and HF, induces chemical reaction with column's stationary phase, trifluoropyl methylpolysiloxane, leading to the formation of corresponding byproducts such as (CH₃)₂SiF₂. While, in the case of COF₂, the peak area value taken from the consecutive measurements was not consistent, and a larger spread was observed for all the concentration ranges from lower to higher concentrations (Figures 3e and 3f). Indicating the instability and reactive behavior of COF₂ molecules in each measurement, that makes it difficult to quantify by a GC-MS instrument.

Furthermore, Table 3 summarizes the response factor (R_p) , regression value, and the standard deviations corresponding to the graphs shown in Figure 3. Typically, the linear regression curve is obtained by plotting the known concentration against the peak area under the curve, derived



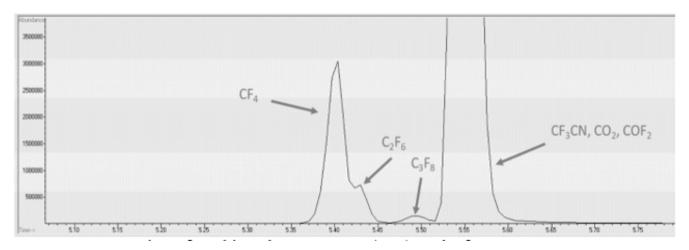


Figure 2: Representation of total ion chromatogram (TIC) peaks for CF₄, C₂F₆, C₃F₈, CF₃CN, and COF₂

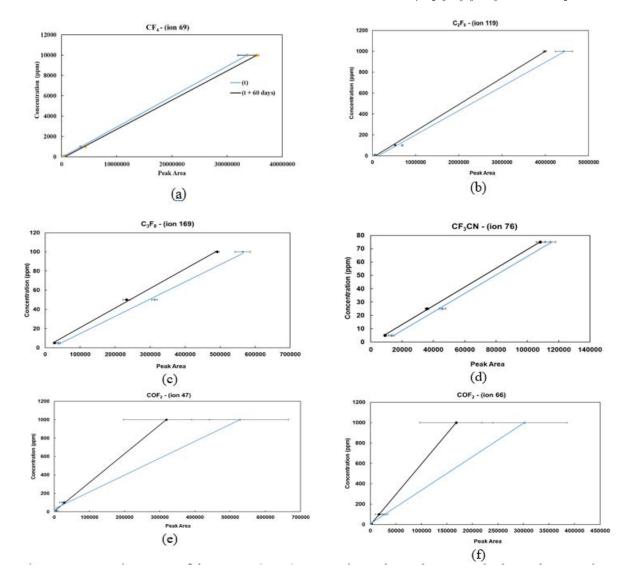


Figure 3: Regression curve of the $C_4F_7N/CO_7/O_2$ gas mixture byproduct's standard samples over time intervals from (t) to (t) + 60 days: (a): CF₄, (b): C₂F₆, (c): C₃F₈, (d): CF₃CN, (e, and f): COF₂

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Table	e 3: Response fa	ctor (slop of the linear co	urve) and the s	tandard deviation of all the cal	ibrated gases over a	i 60-day period
_		(R.) response factor.	Regression	(R.) response factor, after		Standard deviat

Molecules	Molecular ion	(R _f) response factor, (a, equation 1) ×10 ⁴)	Regression (R²)	(R _s) response factor, after 60 days (a, equation 1) ×10 ⁴	Regression (R²)	Standard deviation (STDEV %)
CF ₄	CF ₃ ⁺ (69)	2.9	0.9999	3	0.9999	2
C ₂ F ₆	C ₂ F ₅ ⁺ (119)	3	0.9963	3	0.9998	3
C ₃ F ₈	C ₃ F ₇ ⁺ (169)	2	0.9968	3	0.998	4
CF ₃ CN	CF ₂ CN ⁺ (76)	7	0.9986	7	0.9997	4
COF	COF+ (47)	1.8	0.9976	1.8	0.9976	60
COF ₂	COF ₂ ⁺ (66)	3.1	0.9999	6	0.9999	69

from multiple measurements. Furthermore, fluorocarbons $(C_nF_{2n+2}, \text{ and } C_nF_{2n})$ have similar values; therefore, they can also be considered to determine the concentration of other fluorocarbons and cyano groups. On average, the standard deviation is calculated by using Equation 2 and for all molecules, it is approximately 4%, except for COF_2 , which is 69% due to the wide dispersion of the peak area in the consecutive measurements (Figure 3e, 3f).

$$STDEV = \sqrt{\frac{\sum (x_i - \vec{x})^2}{n-1}}$$
 (2)

$$u(c) = \sqrt{S_{avg}^2 \left(\frac{(u(a))}{\sqrt{3}}\right)^2 + \left(\frac{(u(b))}{\sqrt{3}}\right)^2 + a_{avg}^2 * (std(S))^2}$$
(3)

Equation 3 illustrates the uncertainty formula used to calculate the uncertainty of the concentration of all byproducts [12]. Where, std(S) is the standard deviation of average area value; u(a) represents the uncertainty in the slope a; u(b) represents the uncertainty in the intercept b and a_{avg} represent the average value of peak area. The significance of the uncertainty values of the byproducts in calibration accounting for errors from instrument variability, environmental factors, and sample inconsistencies. They ensure accuracy, regulatory compliance, and confidence in the quantitative results of polluted $C_4F_7N/CO_2/O_2$ gas mixture samples in the industrial settings.

COF, quantification using FTIR

The higher standard deviation and uncertainty of COF_2 prompted us to develop its methodology by FTIR. A constant pressure of 1000 mbar gas was filled in the gas cell, maintained by the Bronkhorst high-tech control valve, and simultaneously obtained four consecutive measurements (Figure 4). Existing literature [14], indicate the range of COF_2 peaks lies between (~1800 - 2000 cm-1). Accordingly, selected the range between 1872.98 cm⁻¹ and 1988.52 cm⁻¹ to calibrate the COF_2 (10, 100, and 1000 ppm) with the classical least squares (CLS) methodology (Figure 4). The regression curve is generated using TQ software (Figure 5).

The COF₂ concentration values obtained from FTIR measurements are less dispersed and more accurate

Table 4: Uncertainty values for standard gas molecules at various concentration

Gas molecules	Concentration (ppm)	Uncertainty u(c) (ppm)	
	1000	4	
CF ₄	10000	41	
	100000	120	
	10	2	
C_2F_6	100	6	
	1000	11	
	5	1	
C_3F_8	50	2.7	
	100	2.7	
	5	0.6	
CF₃CN	25	0.9	
	75	2	
	10	8.2	
COF ₂ (ion 47)	100	17	
	1000	26	
	10	6.5	
COF ₂ (ion 66)	100	16	
	1000	250	

(Table 4). Therefore, based on these measurements, the quantitative results of the standard gas bottles confirm the COF₂ measurement via FTIR technology is more effective than GC-MS, where the standard deviation is 69% (Table 3).

Moreover, in a heavily polluted $C_4F_7N/CO_2/O_2$ gas mixture sample, the high COF_2 concentration caused peak saturation in the infrared spectrum; therefore, dilution with decreasing the pressure below 1000 mbar must be adjusted before taking the right concentration value in a sample.

Furthermore, due to the limitation of the experimental study, the density functional theory (DFT) [15], must be employed to develop the model and to compare the analytical results with the established possible chemical reaction mechanism.



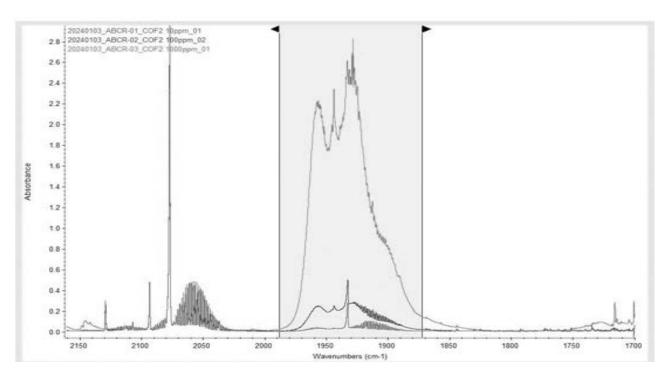


Figure 4: Selected region for COF₂ calibration in the range of (10, 100 and 1000) ppm concentration within the wavelength of (1872.98 - 1988.52) cm⁻¹

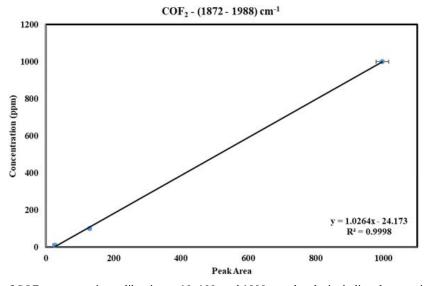


Figure 5: Illustration of COF2 concentration calibration at 10, 100, and 1000 ppm levels, including the associated standard deviations

Table 5: Comparison of COF₂ standard sample measurements results using GC-MS and FTIR instruments

#	Measurement results by GC-MS (ppm)			Measurement results via FTIR (ppm)	
	COF ₂ (ppm)	GC-MS (ion - 47)	GC-MS (ion - 66)	Standard deviation (%)	FTIR (after 4 months)
Bottle 1	10	54	32	69	4.3 ± 0.5
Bottle 2	100	96	88		98 ± 3
Bottle 3	1000	514	513		937 ± 25

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Conclusion

Detection and quantification of polluted decomposition byproducts with the help of GC-MS and FTIR technology is crucial to increase knowledge on the byproduct identification and quantification. In this regards, optimum GC-MS methodology is established, and calibration of gases including CF₄, C₂F₆, C₃F₈, COF₂, and CF₃CN is performed. Complete peak separation with adjusting parameters was not possible in our case due to the matrix effect, and an injection flow rate of 3 mL/min was found to be optimal for partial peak separation. Slight movement of the regression curve of all molecules is observed, indicating the degradation of the column stationary phase. COF, calibration via GC-MS is not achievable due to the significant variation of the peak area values in the consecutive measurements and attributed to the corrosive nature of COF₂, as it can react easily with the columns stationary phase. COF, calibration by FTIR is reliable in our case, and the standard deviation of COF, from FTIR calibration was around 4%; that was 69% in the case of GC-MS. A total of 15 byproducts are detected by GC-MS in the polluted sample, including CO, $\begin{array}{l} \text{CF}_4, \text{C}_2\text{F}_6, \text{C}_3\text{F}_8, \text{C}_2\text{F}_4, \text{C}_3\text{F}_6, \text{COF}_2, \text{CF}_3\text{CN}, \text{C}_2\text{F}_5\text{CN}, \text{CF}_2\text{=CF-CN}, (\text{CN})_2, \text{CF}_3\text{-N=CF}_2, \text{CF}(\text{CF}_3)_2\text{-CO-NH}_2, \text{and } (\text{CH}_3)_2\text{SiF}_2. \end{array}$ The byproducts generation during arcing coming from gas mixture decomposition of course but the ablation phenomena of PTFE nozzle induce at the same time the generation of fluorocarbon byproducts. Understanding the chemical composition of the gas mixture is essential and has been used to define and implement appropriate environmental and health safety procedures.

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