

# Exploring the Decomposition Products of 1,3,3,3-Tetrafluoropropene and Perfluoro-(3-methylbutan-2-one) Gas Mixtures in Medium-Voltage Electrical Switchgear as Alternatives to SF<sub>6</sub>

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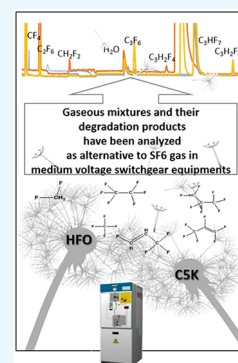
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**ABSTRACT:** In this work, binary and ternary gas mixtures of 1,3,3,3-tetrafluoropropene, HFO-1234ze(E), and perfluoro-(3-methylbutan-2-one),  $\text{CF}_3\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ , with  $\text{CO}_2$  and synthetic air, are presented as alternatives to  $\text{SF}_6$  in medium-voltage electrical equipment. They were used in four medium-voltage switchgear cubicles replacing  $\text{SF}_6$  gas, and after a period of time, under permanent 30 kV AC voltage, gas mixture samples were extracted and analyzed on the same day using a validated methodology based on gas chromatography (GC) coupled to mass spectrometry (MS) and thermal conductivity (TCD).  $\text{CF}_4$  (tetrafluoromethane),  $\text{C}_2\text{F}_6$  (hexafluoroethane),  $\text{C}_3\text{F}_6$  (hexafluoropropylene),  $\text{C}_3\text{HF}_7$  (1,1,1,2,2,3,3-heptafluoropropane),  $\text{CH}_2\text{F}_2$  (difluoromethane), and the cis and trans- $\text{C}_3\text{H}_2\text{F}_4$  (1,3,3,3-tetrafluoropropene) have been identified as decomposition products in these gas mixtures. In addition, a quantity of water has been observed, as well as CO in one of the cubicles. The most abundant decomposition products identified in gas mixture samples ( $\text{C}_3\text{HF}_7$  and  $\text{C}_3\text{F}_6$ ) together with water and CO content have been quantified using commercial gas mixture reference standards. The toxicity and global warming of the analyzed compounds are evaluated to determine the most adequate gas mixture among those studied as a candidate to substitute  $\text{SF}_6$ .



## 1. INTRODUCTION

Nowadays, manufacturers of medium-voltage switchgear frequently use sulfur hexafluoride ( $\text{SF}_6$ ) in the equipment because of its very good insulation and switching properties.  $\text{SF}_6$  has unique characteristics such as relatively low toxicity, extreme inertness, and high dielectric strength. However,  $\text{SF}_6$  is one of the most potent greenhouse gases that cause significant global warming, 23,500 times higher than  $\text{CO}_2$ , according to IPCC's Fifth Assessment Report (AR5).<sup>1–3</sup>

Although there are other insulating technologies (oil or solid insulation), they present drawbacks because of safety or cost issues, making gas insulation the best choice for distribution switchgears. Therefore, there is a need for a gaseous alternative, that is, gas or gas mixture, which can replace  $\text{SF}_6$  in medium-voltage electrical equipment. Alternative gas or gas mixtures must have an acceptable combination of low boiling point, chemical stability, nonflammability, high dielectric strength, and as low as possible global warming potential (GWP), at least less than 150, based on the Annex III of Regulation (EU) No. 517/2014 of the European Parliament and of the Council of 16 April 2014. This regulation has been established for fluorinated greenhouse gases used in foams, refrigerators, and freezers that contain HFCs (hermetically sealed equipment), movable room air-conditioning equipment or technical aerosols.

In addition, alternative gas mixtures must have relatively low toxicity, and depending on the specific application, they should be functional at temperatures as low as  $-25\text{ }^\circ\text{C}$  or even as low as  $-30\text{ }^\circ\text{C}$ .<sup>3,4</sup>

Investigations have been focused on natural gases ( $\text{N}_2$ ,  $\text{CO}_2$ , and dry air) and more recently on new halogenated products with low GWP such as trifluoroiodomethane ( $\text{CF}_3\text{I}$ ), perfluorinated ketones, hydrofluoroolefins, and fluoronitriles.<sup>5–8</sup>

Ormazabal Corporate Technology has found that gas mixtures with hydrofluoroolefins such as 1,3,3,3-tetrafluoropropene HFO-1234ze(E) (HFO) and perfluoroketones such as perfluoro-(3-methylbutan-2-one)  $\text{CF}_3\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$  (CSK) can be environmentally and economically feasible for their use in medium-voltage electrical distribution switchgear (from 12 to 40.5 kV), reaching similar values of electrical stiffness to that of  $\text{SF}_6$ . Unfortunately, these polyfluorinated gases have a boiling point higher than  $\text{SF}_6$ , Table 1, which is a

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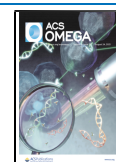


Table 1. Physicochemical Properties of HFO and C5K in Comparison with SF6

	SF6 [6]	HFO (HFO-1234zeE) [6, 9]	C5K [6, 9, 10]
molecular structure			
molecular weight (g/mol)	146	114	266
boiling point (°C)	-63	19.4	26
dielectric strength (%SF6)	100 %	85 %	140 %
GWP (100 years)	23.500	1	1
acute toxicity (LC50 4 h/rat, ppmv)	>500000	>200000	>20000
chronic toxicity (TWA, ppmv)	1000	800	225
flammability	non-flammable	midly-flammable	non-flammable

drawback for their use in low-temperature applications of medium-voltage switchgear. However, the addition of dry air, nitrogen, or carbon dioxide in the gas mixtures reduces the boiling points of their mixtures, and they can also inhibit the formation of some decomposition products.

HFO-1234zeE has good dielectric strength properties, as can be seen in Table 1, and its GWP is less than 1, according to IPCC Fifth Assessment Report [1]. This value is better than that of SF6 (GWP of 23.500). The insulation properties of HFO-1234ze(E) are close to those of SF6 and can probably be used in its pure state for replacing SF6 in medium-voltage applications.<sup>4,5</sup>

Perfluoroketones can be used as an additive to natural gases such as N<sub>2</sub>, CO<sub>2</sub>, or dry air, but their concentration in the mixture will be limited by the minimal operation temperature of the electrical switchgear-specific application.

Some perfluoroketones such as C5K are substantially nontoxic in the pure state and present high insulation capabilities, in particular, a high dielectric strength (or breakdown field strength), and, at the same time, an extremely low GWP (see Table 1). Indeed, by adding fluorine in the chemical formulation of perfluoroketones, the dielectric strength of the complex molecule is improved. In contrast, the boiling point increases considerably.<sup>5–9</sup>

The toxicity of these gases (collected in Table 1) is defined as the acute toxicity (LC50) and chronic toxicity. Low values of LC50 correspond to high gas toxicity. HFO and C5K have high LC50 values, corresponding to category 4 (very low acute toxicity) for HFO (as well as SF6) and category 5 (gas to be taken care of) for C5K, according to the National Institute of Workers.<sup>6</sup> Chronic toxicity is characterized by the threshold limit values time-weighted average (TLV-TWA). The TLV-TWA must be higher than the maximum value that can occur permanently in a factory in normal conditions because of normal leakage during gas handling. It should be higher than 50 ppmv in order to be used in switchgear factories.<sup>9</sup> HFO and C5K satisfy this factor.

The study of the behavior of HFO and C5K mixtures and their possible decomposition products at 30 kV in medium-voltage electrical switchgear requires the development of a suitable analytical method for their monitorization. Gas chromatography (GC) coupled to mass spectrometry (MS), flame ionization (FID), or thermal conductivity (TCD) detectors<sup>3,5–15</sup> have been the analytical techniques frequently chosen for this purpose. Two-dimensional (2D) chromatography has been preferentially used to perform an optimal

separation of the chromatographic peaks, but good resolution has not been obtained.

Therefore, the aim of this work is to study the chemical stability of different gas mixtures of dielectric gases, such as HFO and C5K, in combination with CO<sub>2</sub> or synthetic air, as alternative gases to SF6, at 30 kV in medium-voltage electrical switchgear. In order to carry out this study, a simple and rapid one-dimensional (1D) chromatographic method with an optimal chromatographic resolution has been developed and validated for the quantitative analysis of gas mixtures with HFO and C5K and their possible decomposition products.

## 2. RESULTS AND DISCUSSION

### 2.1. Chromatographic Behavior of HFO and C5K Gases.

In Figure 1, the GC/MS and GC/TCD chromatograms of 40% v/v HFO in synthetic air and 20% v/v C5K in synthetic air.

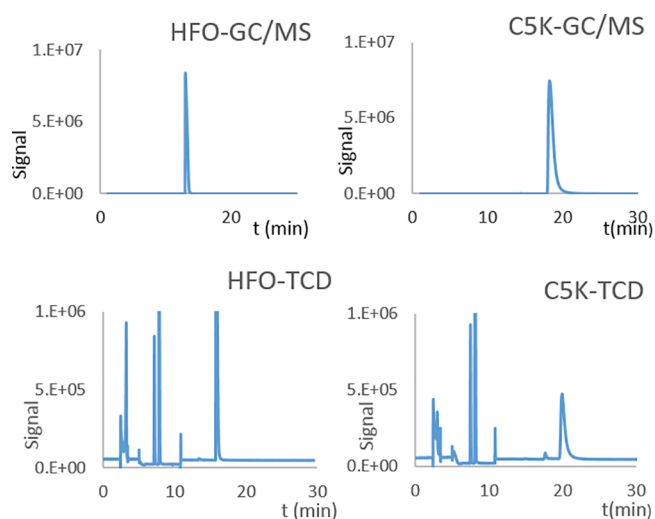


Figure 1. GC/MS and GC/TCD chromatograms of 40% v/v HFO in synthetic air and 20% v/v C5K in synthetic air.

grams of HFO and C5K reference gases, obtained under the conditions optimized are shown. Table 2 shows the retention times (*t<sub>r</sub>*) and characteristic ions (*m/z*) of the studied compounds.

**2.2. Validation of the Chromatographic System.** Once chromatographic conditions were optimized to achieve a good chromatographic resolution of the two reference gases for both chromatographic systems used (GC/MS and GC/TCD), validation of the analytical method was carried out in terms

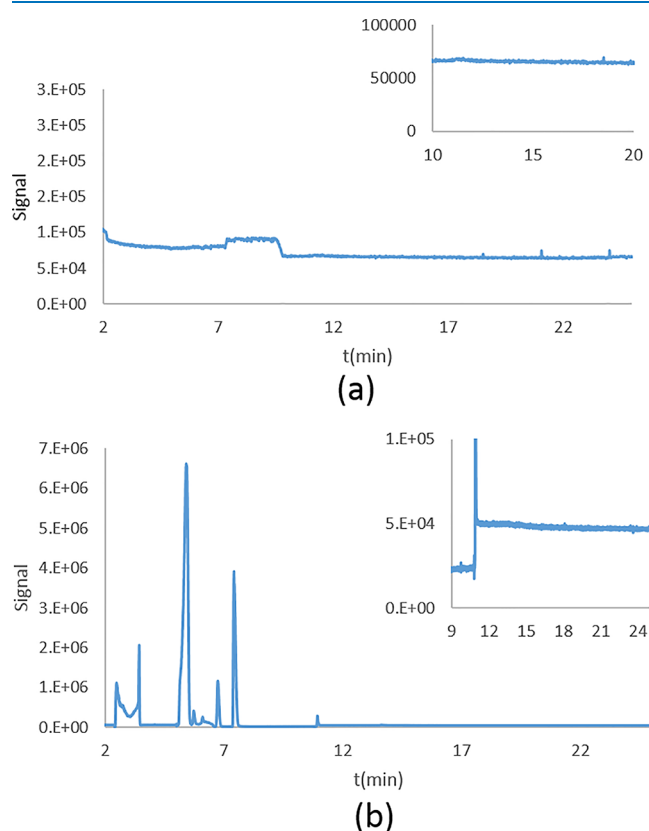
**Table 2. Retention Times ( $t_r$ ) and Characteristic  $m/z$  Ions of the Studied Compounds Obtained by GC/MS and GC/TCD Chromatographic Systems<sup>a</sup>**

Analyte	GC/TCD $t_r$ (min)	GC/MS $t_r$ (min)	$m/z$
HFO	16	13.5	64, 69, 95, <b>114</b>
C5K	20	18.5	<b>69</b> , 97, 169, 197

<sup>a</sup>Ions in bold are used for quantification.

of selectivity, limit of detection (LOD) and quantification (LOQ), linear concentration range, and intermediate precision.

**2.2.1. Selectivity.** The selectivity parameter determines whether a chromatographic peak is only due to the analyte of interest and not to the presence of interferences in the sample. As can be seen in Figure 2, chromatographic peaks do not appear in the blank sample (synthetic air) at the retention times of the two analytes (Table 3).



**Figure 2.** Synthetic air chromatograms obtained by GC/MS (a) and by GC/TCD systems (b).

**2.2.2. Limit of Detection and Quantification.** The lowest concentration of the analyte that can be detected using the method at a specified level of confidence is named the LOD. The LOD refers to the qualitative aspect of the method but does not refer to whether the analyte can be reliably quantified. For this purpose, the LOQ is additionally required. The LOQ is defined as the minimum amount of analyte that can be quantified with an acceptable level of precision and accuracy. A signal/noise ratio (S/N) was used for the LOD and LOQ. A

**Table 3. LOD and LOQ Values (% v/v) and Variation of Response with C5K and HFO Concentrations for GC/MS and GC/TCD Systems**

Technique	Analyte	LOD (% v/v)	LOQ (% v/v)	Linear Response
GC/MS	HFO	0.22	0.32	$y=2362935x$
	C5K	0.13	0.19	$y=18525083x$
GC/TCD	HFO	0.21	0.27	$y=544799x$
	C5K	0.39	0.50	$y=609046x$

S/N value of 3 for LOD and S/N of 10 for LOQ are acceptable.

**2.2.3. Linear Concentration Range.** The ability of an analytical method to give responses that are proportional to the amounts of an analyte in a sample determines its linear concentration range. Different gas mixtures composed of different percentages of C5K and HFO with synthetic air were prepared in a stainless-steel cylinder in order to create different calibration standards. These calibration standards were stored in Tedlar bags until analysis. In Table 3, the linear regression equations obtained when the chromatographic peak area and gas concentration data were treated for GC/MS and GC/TCD are collected. The linear concentration range obtained was from LOQ to 20% v/v for C5K and LOQ to 40% v/v for HFO.

**2.2.4. Intermediate Precision.** Two types of precision were determined: intraday analyses in working sessions of 6 replicates and interday analyses in 6 nonconsecutive working sessions (one per month).

Two different concentrations (20 and 3% v/v for C5K and 5 and 40% v/v for HFO) were assayed for each gas in the precision study. The results are expressed as the relative standard deviation (RSD %) in Table 4. RSD% values lower than 7.5% were obtained for both concentrations, which show the precision of the analytical method developed.

**Table 4. RSD% Values Obtained for the Intermediate Precision for HFO and C5K**

Technique	Analyte	Intra-day precision %RSD	Inter-day precision %RSD
GC/MS	40% HFO	5.6	6.2
	5% HFO	7.3	7.0
	20% C5K	6.6	6.9
	3% C5K	2.5	3.0
GC/TCD	40% HFO	4.5	5.4
	5% HFO	4.7	5.7
	20% C5K	4.4	5.2
	3% C5K	3.7	4.5

**2.2.5. Identification of Decomposition Products Formed in the Medium-Voltage Electrical Switchgear.** Different gas mixtures of HFO and C5K in combination with synthetic air or CO<sub>2</sub> were selected as alternative gas mixtures to fill the cubicles of the four medium-voltage switchgears.

A permanent 30 kV AC voltage was applied to the four prototype MV switchgear cubicles to check the stability of these four gas mixtures under operating conditions in the electrical switchgear. For this purpose, the Ormazabal Corporate Technology's experimentation network called UDEX (Demonstration and Experimentation Unit) has been used.<sup>16,17</sup> This network is a highly configurable medium-

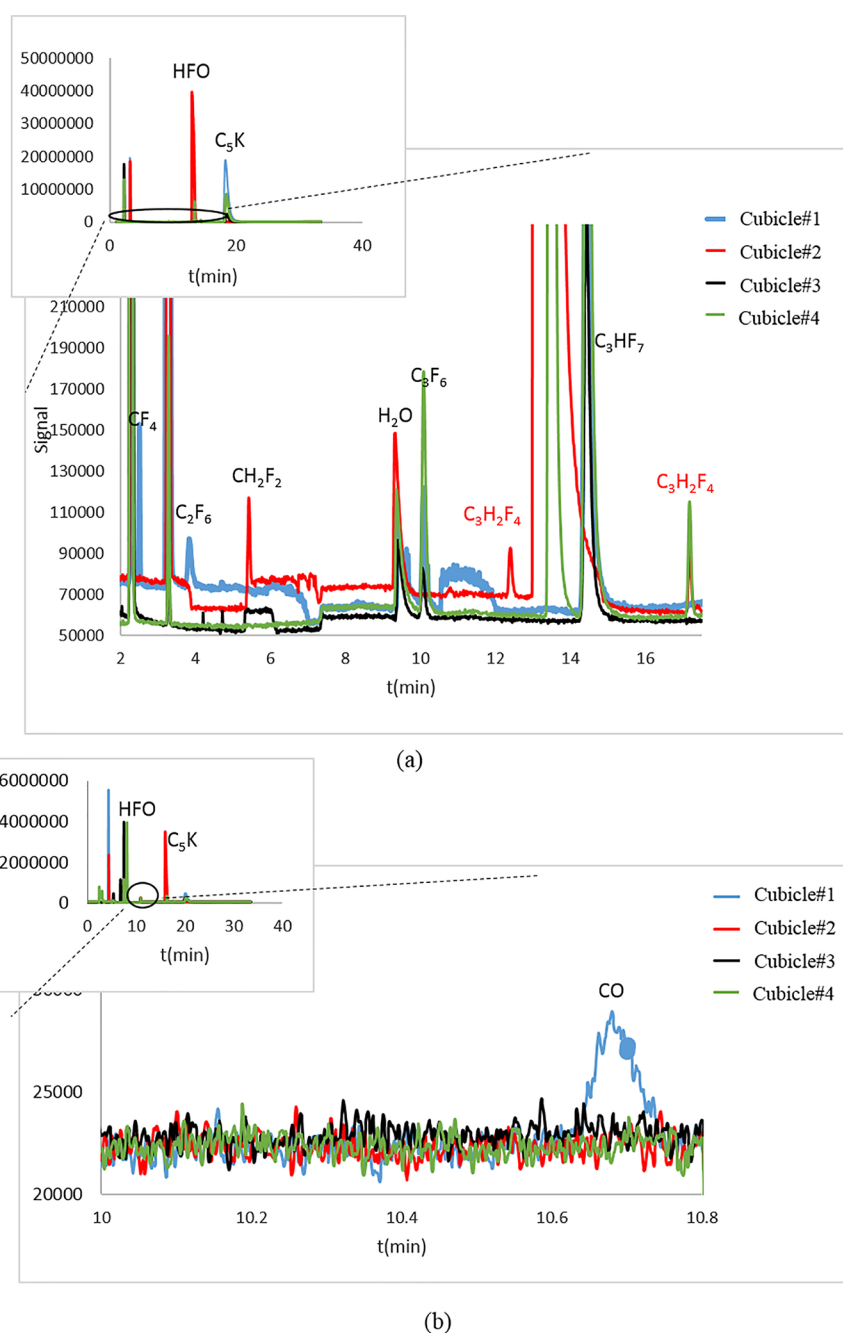


Figure 3. Chromatograms of samples analyzed (a) by GC/MS and (b) by GC/TCD.

Table 5. Decomposition Compounds Identified in the Samples Studied


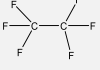
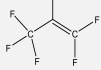
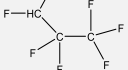

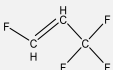
	Gas mixture	Decomposition products
<b>Cubicle #1</b>	20% C5K + CO <sub>2</sub>	CO, H <sub>2</sub> O, CF <sub>4</sub> , C <sub>2</sub> F <sub>6</sub> , C <sub>3</sub> F <sub>6</sub> , C <sub>3</sub> HF <sub>7</sub>
<b>Cubicle #2</b>	78% HFO + CO <sub>2</sub>	H <sub>2</sub> O, CH <sub>2</sub> F <sub>2</sub> , cis-C <sub>3</sub> H <sub>2</sub> F <sub>4</sub>
<b>Cubicle #3</b>	10% C5K + synthetic air	H <sub>2</sub> O, C <sub>3</sub> F <sub>6</sub> , C <sub>3</sub> HF <sub>7</sub>
<b>Cubicle #4</b>	10% C5K + 3% HFO + synthetic air	H <sub>2</sub> O, C <sub>3</sub> F <sub>6</sub> , C <sub>3</sub> HF <sub>7</sub> , cis-C <sub>3</sub> H <sub>2</sub> F <sub>4</sub>

voltage network independent from the grid, which allows the development and testing of new technologies, products, and services in a safe and controlled environment.

Both developed analytical methods were used for the quantification of C5K and HFO and for the detection, identification and, in some cases, quantification of decomposition products generated in the gas mixtures in the cubicles



Table 6. Retention Times (tr) and Physicochemical Properties of Identified Decomposition Compounds

	degradation compounds of C5K				degradation compounds of HFO	
	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	C <sub>3</sub> F <sub>6</sub>	C <sub>3</sub> HF <sub>7</sub>	CH <sub>2</sub> F <sub>2</sub>	Cis-C <sub>3</sub> H <sub>2</sub> F <sub>4</sub>
t <sub>r</sub> (min)	2.50	3.85	10.0	14.5	5.5	17.19
chemical formula						
molecular weight (g/mol)	88	138	150	170	52	114
GWP (100 years)	7390	12200	<5	2900	675	1
toxicity (LC <sub>50</sub> 4 h/rat, ppmv)	89500*	40000	1672	non toxic	>520000	>200000
flammability	non-flammable	non-flammable	non-flammable	non-flammable	flammable	low-flammable

\*Value referred to 15 months.

after being under permanent 30 kV AC voltage during a long time interval (4 years in cubicle #1 and 1.5 years in cubicles #2, #3, and #4).

In Figure 3, chromatograms of the gas samples of the identified compounds are shown. The initial compositions of HFO and C5K in gas mixtures used in the four medium-voltage cubicles and identified decomposition products are indicated in Table 5.

CF<sub>4</sub> (tetrafluoromethane), C<sub>2</sub>F<sub>6</sub> (hexafluoroethane), C<sub>3</sub>F<sub>6</sub> (hexafluoropropylene), and C<sub>3</sub>HF<sub>7</sub> (1,1,1,2,2,3,3-heptafluoropropane) are the degradation products from the C5K.

CF<sub>4</sub> may be narcotic at high concentrations, thermally stable, and chemically very inert.<sup>6,18–20</sup> C<sub>2</sub>F<sub>6</sub> is relatively inert, nonflammable, and nontoxic, although asphyxiation may occur because of the displacement of oxygen.<sup>6,18,21,22</sup> C<sub>3</sub>F<sub>6</sub> is noncombustible, and it can asphyxiate by the displacement of air, may cause respiratory irritation, moderately or very reactive, and may be incompatible with many amines, nitrides, azo/diazo compounds, alkali metals, and epoxides.<sup>6,18,23</sup> C<sub>3</sub>HF<sub>7</sub> is heavier than air, and it may asphyxiate by the displacement of air, especially in a confined space. It does not react rapidly with air and with water. It may be incompatible with many amines, nitrides, azo/diazo compounds, alkali metals, and epoxides.<sup>6,18,21,22</sup> CF<sub>4</sub> and C<sub>3</sub>F<sub>6</sub> appear in bibliography as moderate or slightly toxic decomposition products.<sup>3,23</sup>

CH<sub>2</sub>F<sub>2</sub> (difluoromethane) and cis-C<sub>3</sub>H<sub>2</sub>F<sub>4</sub> (1,3,3,3-tetrafluoropropene) are degradation products from hydrofluoroolefin. CH<sub>2</sub>F<sub>2</sub> has high thermal stability. Its vapors are heavier than air. Under prolonged exposure to fire or intense heat, the containers may rupture violently and rocket.<sup>6,24</sup> Cis and trans C<sub>3</sub>H<sub>2</sub>F<sub>4</sub> are less flammable than the mixture of both cis and trans isomers.<sup>25,26</sup>

The physicochemical properties of these degradation compounds are summarized in Table 6, with the retention times and chemical formula.

In view of the decomposition products that are formed and their abundance, the breakage of the C–C bond between C1 and C2 atoms of HFO and C5K (Table 1) is more likely to occur. This reaction generates CH<sub>2</sub>F<sub>2</sub> for HFO and C<sub>3</sub>F<sub>6</sub> y C<sub>3</sub>HF<sub>7</sub> for C5K.

In the case of C5K, the C<sub>3</sub>F<sub>6</sub> y C<sub>3</sub>HF<sub>7</sub> compounds react further to produce CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>. Studies carried out by different authors<sup>27–30</sup> corroborate the formation of the degradation products identified in our experiments for C5K.

Degradation pathways according to the density functional theory (DFT) and modeling studies have been proposed in the literature for C5K. Furthermore, Wang, Y. et al.<sup>27</sup> reported that C5K generates less CO with air mixtures and more oxygenated chemicals. However, under the conditions used in this work, CO or any other oxygenated compound is not produced in mixtures with air. CO is only generated in the CO<sub>2</sub> medium. In addition, Zhang, Y. et al.<sup>30</sup> reported that in the presence of O<sub>2</sub>, the formation of large molecules is inhibited and compounds with double bonds, such as C<sub>3</sub>F<sub>6</sub>, are not stable. Nevertheless, in this study, this compound is one of the major products. Therefore, the formation of decomposition products depends on the conditions of temperature, pressure, and voltage to which the gas mixtures are subjected.

The potential for all these degradation products of C5K and HFO to cause cancer in humans has not been assessed by the U.S. EPA IRIS program, the International Agency for Research on Cancer, or the U.S. National Toxicology Program 14th Report on Carcinogens (SRC).<sup>31,32</sup> On the other hand, highly fluorinated compounds are not expected to biodegrade rapidly.<sup>33,34</sup>

The possible causes of these degradation products could be due to the influence of electrical field present in the cubicles and the interaction of compounds in the gas mixtures with water coming from HFO and from some plastic materials present inside the cubicles.

To evaluate if these decomposition products are acceptable for the adequate performance of the cubicles in an installation under real operating conditions over the entire life duration (30 years) is a more complex issue and requires more long-life assessments to check the behavior over time. New samples are expected to be extracted after an additional long period of time to follow the evolution of gas mixture compositions. Dielectric and mechanical type tests will have to be performed to the cubicles after a longer time to evaluate the influence of these new gas mixtures on the technical functionality of the medium-voltage switchgear cubicles.

After the identification of the degradation compounds produced in the different mixtures, the concentrations of the most abundant compounds (C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>HF<sub>7</sub>) were obtained by GC/MS using a commercial gas mixture reference standard of 500 ppmv of each gas (C<sub>3</sub>HF<sub>7</sub>–CO–C<sub>3</sub>F<sub>6</sub>–He), Table 8.

Furthermore, CO and water contents were analyzed in gas samples by GC/TCD and GC/MS, respectively, Table 7, using H<sub>2</sub>O (50 ppmv) and CO (500 ppmv) reference standards.

H<sub>2</sub>O is analyzed because of its possible problem of generating degradation compounds and CO due to its toxicity.

**Table 7. Concentration of CO, H<sub>2</sub>O, C<sub>3</sub>F<sub>6</sub>, and C<sub>3</sub>HF<sub>7</sub> in the Samples Studied**

Samples	CO (ppmv)	H <sub>2</sub> O (ppmv)	C <sub>3</sub> F <sub>6</sub> (ppmv)	C <sub>3</sub> HF <sub>7</sub> (ppmv)
Cubicle #1	1016	61	201	1911
Cubicle #2	<500	81	<100	<100
Cubicle #3	<500	64	432	4491
Cubicle #4	<500	63	408	2688

Calibration curves, Table 8, for the acquired gas mixture reference standard of C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>HF<sub>7</sub> were built from 0.01 to

**Table 8. Variation of Response with the Concentration of C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>HF<sub>7</sub> by GC/MS**

Technique	Analyte	Linear Response
GC/MS	C <sub>3</sub> F <sub>6</sub>	y=4E06x r <sup>2</sup> =0.9927
	C <sub>3</sub> HF <sub>7</sub>	y=8E06x r <sup>2</sup> =0.9912

0.05% v/v, using the splitless mode in the GC/MS equipment and injecting a higher sample volume (0.5 mL).

Small quantities of weakly toxic C<sub>3</sub>F<sub>6</sub> (≤0.04%), C<sub>3</sub>HF<sub>7</sub> (≤0.4%), and a certain amount of CO (≤1%), H<sub>2</sub>O (≤0.006%) have been found in the mixtures.

**2.3. Interlaboratory Studies.** For further validation of the analytical method, an interlaboratory assay was carried out for C5K and the most abundant degradation compounds (C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>HF<sub>7</sub>). Gas samples of three of the four cubicles (#1, #3, and #4) were extracted 3 months later than the gas samples analyzed in our laboratory. They were collected in this case in 500 cm<sup>3</sup> stainless-steel cylinders to be sent to 3M Analytical Laboratory in USA.

3M Analytical Laboratory used GC-FID as the analytical technique and a semiquantitative method to calculate the C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>HF<sub>7</sub> contents in gas samples. C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>HF<sub>7</sub> concentrations were calculated by dividing their GC-FID chromatographic signal area by the chromatographic signal

area of C5K, and the result was multiplied by the known concentration of C5K in the gas sample. The calculated values are shown in Table 9.

The results obtained in 3M laboratory appear to be very consistent with those obtained using the analytical method developed by our research group.

Additionally, the concentrations of the gas mixtures after these periods of electrical aging (4 years and 1.5 years) are very similar to the initial ones, and the four cubicles withstand 30 kV perfectly. In addition, the pressure of the gas mixtures in the cubicles is maintained (there are no abnormal leaks).

### 3. CONCLUSIONS

The analytical methodology for monitoring the chemical stability of dielectric gas mixtures at 30 kV in medium-voltage switchgear has been successfully developed and validated. In addition, the interlaboratory assay carried out has allowed us to obtain no significant differences in the results obtained by the two laboratories: UPV/EHU and 3M laboratory.

With the methodology validated, the decomposition products of gas mixtures of C5K and HFO with synthetic air and CO<sub>2</sub> have been identified. CF<sub>4</sub> (tetrafluoromethane), C<sub>2</sub>F<sub>6</sub> (hexafluoroethane), C<sub>3</sub>F<sub>6</sub> (hexafluoropropylene), and C<sub>3</sub>HF<sub>7</sub> (1,1,1,2,2,3,3-heptafluoropropane) are the degradation products from C5K, and CH<sub>2</sub>F<sub>2</sub> (Difluoromethane) and trans-C<sub>3</sub>H<sub>2</sub>F<sub>4</sub> (1,3,3,3-Tetrafluoropropene) are the degradation products from HFO.

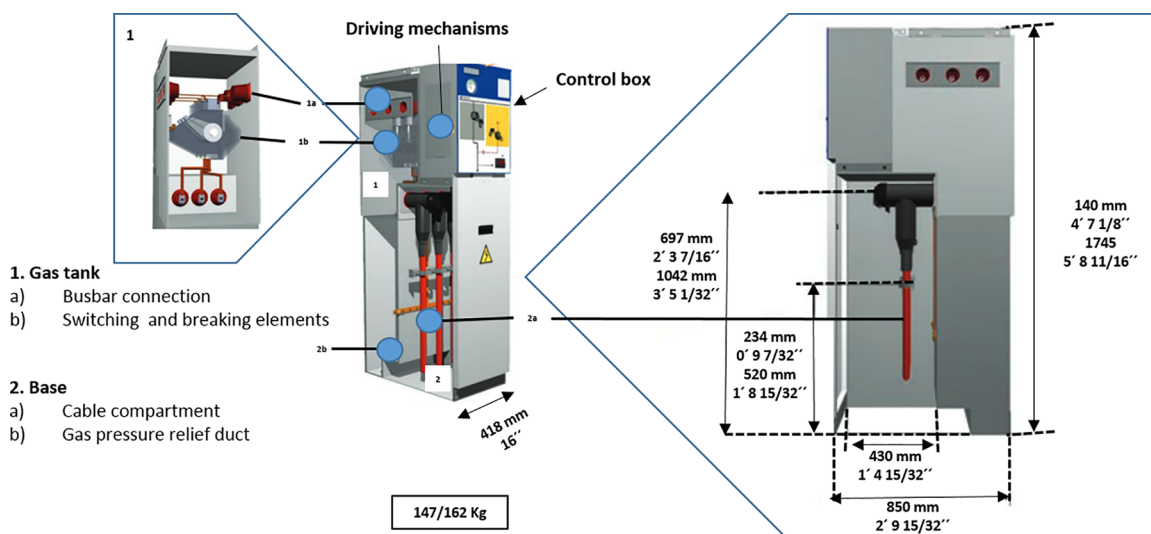
In this work, small quantities of weakly toxic C<sub>3</sub>F<sub>6</sub> (≤0.04%), C<sub>3</sub>HF<sub>7</sub> (≤0.4%), and a certain amount of CO (≤1%) and H<sub>2</sub>O (≤0.006%) have been found.

It is possible that part of C<sub>3</sub>HF<sub>7</sub> dehydrofluorinates to form C<sub>3</sub>F<sub>6</sub>. The presence of C<sub>3</sub>HF<sub>7</sub> in samples of gas mixtures with C5K can be explained from a reaction of fluoroketone C5K with the humidity present in plastics of the cubicle (for example, some polyamides).

One step to prevent the formation of these degradation products would be to avoid the presence of water within the cubicle. On the one hand, HFO contains humidity. On the other hand, the plastic components of the cubicles are polyamides, which contain 4% of water. Anyway, taking into account the values of GWP and LC50 (Table 6), the authors consider that the concentration levels of degradation products are acceptable in terms of toxicity. At any rate, using adequate

**Table 9. Results of the Interlaboratory Assay Carried Out by Basque Country University (UPV/EHU) and 3M Analytical Laboratory**

Cubicle	Gas mixture	UPV/EHU (GC-MS)			3M Analytical Laboratory (GC-FID)		
		% C5K	% C <sub>3</sub> F <sub>6</sub>	% C <sub>3</sub> HF <sub>7</sub>	% C5K	% C <sub>3</sub> F <sub>6</sub>	% C <sub>3</sub> HF <sub>7</sub>
Cubicle #1 4 years with 30kV	20% C5K + CO <sub>2</sub>	19.46	0.02	0.19	18.93	0.02	0.19
Cubicle #3 1.5 years with 30kV	10% C5K + air	9.88	0.04	0.45	8.35	0.04	0.58
Cubicle #4 1.5 years with 30kV	10% C5K + 3% HFO +air	10.28	0.04	0.27	10.49	0.04	0.35



**Figure 4.** Dimensions of the medium-voltage switchgear cubicles used.

adsorbing or absorbing materials, such as molecular sieve, could eliminate water from the gas mixture rapidly to avoid its reaction with CSK. However, the total reduction of water content is not possible because of the active surface properties of molecular sieve. Other alternative would be to use materials that do not retain humidity such as fluoro-elastomer rubber or butyl rubber.

All gas mixtures may be suitable as an alternative to SF<sub>6</sub> because the low proportion of the decomposition products obtained do not represent a health or environmental problem. However, more long-life assessments to check the behavior over time of these decomposition products will be needed.

#### 4. MATERIAL AND METHODS

**4.1. Reagents.** HFO was supplied by Inventec Performance Chemicals (Saint-Priest, France). Purity  $\geq 99.5\%$  weight. Moisture content  $\leq 50$  ppm weight and nonvolatile residue  $\leq 50$  ppm weight. CSK was obtained from 3M (Minnesota, USA). Purity 99.5%. CO<sub>2</sub> and synthetic air were supplied by Carbueros Metalicos and Air Liquid (Madrid, Spain) and were used as dilution gases for preparing the calibration curves of the different dielectric gases assayed. The decomposition products CO, C<sub>3</sub>F<sub>6</sub>, and C<sub>3</sub>HF<sub>7</sub> were acquired as a mixture of 500 ppmv of each gas in He (CO–C<sub>3</sub>HF<sub>7</sub>–C<sub>3</sub>F<sub>6</sub>–He) from Air Liquid (Madrid, Spain) to be used as a gas reference standard. Finally, an additional gas reference standard with 50 ppmv of water (H<sub>2</sub>O/N<sub>2</sub>.B10.IMP) has been obtained from Air Liquid (Madrid, Spain). Degradation products are of crystal quality, recommended for calibrating analyzers and adjustment equipment for instrumentation, and with a manufacturing tolerance between 5 and 10% and an uncertainty between 2 and 5%.

**4.2. Instrumentation.** GC analysis was performed using a gas chromatograph Agilent 7820A (California, USA), equipped with MS and TCD detectors (5975C and G4332A, respectively).

**4.3. Chromatographic Conditions.** A GC equipment with two injectors was used in this work. One is connected to a column Poraplot Q (25 m  $\times$  0.25 mm  $\times$  8  $\mu$ m) and an MS detector. The other injector is joined to two columns in serial connection, a capillary column HP-PlotQ (30 m  $\times$  0.53 mm  $\times$  40  $\mu$ m) and the other one is a HP-Molesieve (30 m  $\times$  0.32

mm  $\times$  12  $\mu$ m). These are connected by a system of one valve that opens and closes to allow the gas sample to pass from one to another, intermittently, until finally communicating with the TCD detector.

The mechanism of this type of column is not only based on the difference in the boiling point/vapor pressure or in polarities but also by the different interactions of the gas with the stationary phase. PoraPLOT Q is a fused silica recommended column for systems that analyze polar and apolar volatile compounds. HP-PLOT Q is a bonded polystyrene-divinylbenzene column. It was specially developed for the separation of targeted nonpolar and polar compounds, including hydrocarbons, CO<sub>2</sub>, methane, air, CO, water, polar solvents, and sulfur compounds (H<sub>2</sub>S). HP-Molesieve columns, made of zeolite, are ideal for many applications, including routine air monitoring for the analysis of fixed and permanent gases: H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, CH<sub>4</sub>, He, Ne, Ar, Kr, Xe, and SF<sub>6</sub>. Therefore, the combination of these columns, together with the detectors, is appropriate to be able to identify any decomposition product of this type of fluorinated gases.

In order to obtain a good sensitivity of the method and a good resolution of chromatographic peaks, the syringe to inject gas without leaks, the liner, the volume to be injected, the split ratio in each system, injector conditions, and the separation temperature ramp were optimized.

The sample was injected into a chromatograph using a Hamilton syringe glue-free HDHT (GR, Switzerland) after sampling from the working Tedlar bags. Volumes of the inserted sample were 0.1 mL at 1:10 split ratio for TCD and 1 mL at 1:55 split ratio for MS, using a liner 5183–4647 (Agilent, California, USA). The temperature of MS and TCD injectors was set at 200 °C and pressure at 2.4 psi and 14 psi, respectively. The oven temperature was programmed with an initial temperature of 40 °C for 5 min, followed by an increase at a rate of 10 °C min<sup>-1</sup> to 75 °C; finally, the oven temperature was increased at a rate of 5 °C min<sup>-1</sup> up to 200 °C.

The analysis of the mass spectra obtained allows identifying the decomposition products by chemical interpretation or comparison with the NIST14 mass spectra database. Mass spectra were collected from  $m/z$  15 to 300 (with an electronic impact ionization source of 70 eV).



**4.4. Sampling.** The four medium-voltage switchgear cubicles used in this experimentation (Figure 1) are manufactured according to international standard IEC 62271–200:2011 “High-voltage switchgear and controlgear-Part 200: AC metal-enclosed switchgear and controlgear for rated voltages above 1 kV and up to and including 52 kV” (<https://webstore.iec.ch/publication/6716>) and IEC 62271–1:2017 “High-voltage switchgear and controlgear-Part 1: Common specifications for alternating current switchgear and controlgear” (<https://webstore.iec.ch/publication/32982>), their rated voltage being 36 kV and their rated current 630A. They all have a hermetic tank made of AISI 304 stainless steel that contains the medium-voltage circuit and that is filled with each gas mixture. Each manufacturer of medium-voltage switchgear has its own designs and models, with some differences in the construction details. The dimensions of the gas tanks where the gas mixtures are contained are shown in Figure 4.

These four medium-voltage switchgear cubicles were filled at 20 °C with four different alternative gas mixtures, with a final absolute pressure of 1400 mbar (Table 10), and subjected to

**Table 10. Gas Mixture Samples Analyzed**

MV switchgear	Gas Mixture
cubicle #1 (4 years at 30kV)	20% C5K + CO <sub>2</sub>
cubicle #2 (1.5 years at 30kV)	78% HFO + CO <sub>2</sub>
cubicle #3 (1.5 years at 30kV)	10% C5K + synthetic air
cubicle #4 (1.5 years at 30kV)	10% C5K + 3% HFO + synthetic air

permanent 30 kV AC voltage. The electric field in the gas tanks is obviously nonhomogeneous, but in critical areas inside (that is, near to epoxy resin busbars), we have calculated that a maximum electric field is 3.41 kV/mm. The dielectric strength of gas mixtures was determined according to the method ASTM D2477 (standard test method for dielectric breakdown voltage and dielectric strength of insulating gases at commercial power frequencies). The four cubicles filled with the four different gas mixtures passed a standardized dielectric test (70 kV AC withstand the voltage test at a power frequency of 50 Hz) without dielectric failure. The cubicles have not been operated during aging, 4 years (cubicle #1) and 1.5 years (cubicles #2, #3, and #4). After this electrical aging time, gas samples were extracted from the cubicles and taken in 500 cm<sup>3</sup> Tedlar bags, Vertex (Barcelona, Spain), to be analyzed on the same day by GC/MS and GC/TCD.

**4.5. Optimization and Validation of GC–MS and GC–TCD Methods.** Optimization of the chromatographic method was carried out. The most suitable conditions for the injection and elution were studied in order to obtain the maximum sensitivity and repeatability, along with an acceptable chromatographic separation in terms of resolution. The optimized method was validated by evaluating the following parameters: selectivity, LOQ, linear concentration range, and intermediate precision. Finally, for further validation of the analytical method, an interlaboratory assay was carried out in collaboration with 3M Analytical Laboratory (Minnesota, USA).

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### Notes

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