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 SF6

María Luz Alonso,* Rosa María Alonso, José Ignacio Lombraña, Jesús Izcara, and Josu Izagirre

ABSTRACT: In this work, binary and ternary gas mixtures of 1,3,3,3-tetrafluoropropene, HFO-1234ze(E), and perfluoro-(3-methylbutan-2-one), CF3C(O)CF(CF3)2 with CO2 and synthetic air, are presented as alternatives to SF6 in medium-voltage electrical equipment. They were used in four medium-voltage switchgear cubicles replacing SF6 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). CF4 (tetrafluoroethane), C2F6 (hexafluoropropylene), C3HF7 (1,1,2,2,3,3-heptafluoropropene), CH2F2 (difluoromethane), and the cis and trans-C3H2F4 (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 (C3HF7 and C3F6) together with water and CO2 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 SF6.

1. INTRODUCTION

Nowadays, manufacturers of medium-voltage switchgear frequently use sulfur hexafluoride (SF6) in the equipment because of its very good insulation and switching properties. SF6 has unique characteristics such as relatively low toxicity, extreme inertness, and high dielectric strength. However, SF6 is one of the most potent greenhouse gases that cause significant global warming, 23,500 times higher than CO2, according to IPCC’s Fifth Assessment Report (AR5).1–3

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 SF6 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 °C or even as low as −30 °C.3,4

Investigations have been focused on natural gases (N2, CO2, and dry air) and more recently on new halogenated products with low GWP such as trifluoroiodomethane (CF3I), perfluorinated ketones, hydrofluorooolefins, and fluoronitriles.5–8

Ormaizabal 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) CF3C(O)CF(CF3)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 SF6. Unfortunately, these polyfluorinated gases have a boiling point higher than SF6, Table 1, which is a...
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-1234ze(E) 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.

Perfluoroketones can be used as an additive to natural gases such as N₂, CO₂, 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, high dielectric strength (or breakdown field strength), and, at the same time, a 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.

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. 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. 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 monitoring. Gas chromatography (GC) coupled to mass spectrometry (MS), flame ionization (FID), or thermal conductivity (TCD) detectors 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 CO₂ 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 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 HFO in synthetic air and 20% v/v C₅K in synthetic air are shown.

| 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, ppmv) | >50000 | >20000 | >20000 |
| chronic toxicity (TWA, ppmv) | 1000 | 800 | 225 |
| flammability | non-flammable | midly-flammable | non-flammable |

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

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. 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.

2.2.3. 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.

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 CO2 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.16,17 This network is a highly configurable medium-

| Table 2. Retention Times (tr) and Characteristic m/z Ions of the Studied Compounds Obtained by GC/MS and GC/TCD Chromatographic Systems |
|---|---|---|
| Analyte | GC/TCD t_r (min) | GC/MS t_r (min) | m/z |
| HFO | 16 | 13.5 | 64, 69, 95, 114 |
| C5K | 20 | 18.5 | 69, 97, 169, 197 |

*Ions in bold are used for quantification.*

| 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.

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

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 |
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.
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 CSK in gas mixtures used in the four medium-voltage cubicles and identified decomposition products are indicated in Table 5.

CF₄ (tetrfluoromethane), C₂F₆ (hexafluoropethane), C₃F₆ (hexafluoropropylene), and C₅HF₂ (1,1,2,2,3,3-heptafluoro-2-propene) are the degradation products from the CSK.

CF₄ may be narcotic at high concentrations, thermally stable, and chemically very inert.⁶,¹⁸,²⁰ C₂F₆ is relatively inert, nonflammable, and nontoxic, although asphyxiation may occur because of the displacement of oxygen.⁶,¹⁸,²¹,²² C₃F₆ 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.⁶,¹⁸,²³ C₅HF₂ 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.⁸,¹⁸,²¹,²² CF₄ and C₂F₆ appear in bibliography as moderate or slightly toxic decomposition products.⁶,²³

CH₂F₂ (difluoromethane) and cis-C₃H₂F₄ (1,3,3,3-tetrafluoropropene) are degradation products from hydrofluoroolfin. CH₂F₂ 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.⁶,²⁴ cis and trans C₃H₂F₄ are less flammable than the mixture of both cis and trans isomers.²⁵,²⁶

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

### Degradation Pathways

Degradation pathways according to the density functional theory (DFT) and modeling studies have been proposed in the literature for CSK. Furthermore, Wang, Y. et al.²⁷ reported that CSK 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 CO₂ medium. In addition, Zhang, Y. et al.³⁰ reported that in the presence of O₂, the formation of large molecules is inhibited and compounds with double bonds, such as C₅F₁₀, 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 CSK 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).³¹,³² On the other hand, highly fluorinated compounds are not expected to biodegrade rapidly.³³,³⁴

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-time evaluations 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 (C₂F₆ and C₃H₂F₄) were obtained by GC/MS using a commercial gas mixture reference standard of 500 ppmv of each gas (C₅HF₂–CO–C₅F₁₀–He), Table 8.

Furthermore, CO and water contents were analyzed in gas samples by GC/TCD and GC/MS, respectively, Table 7, using H₂O (50 ppmv) and CO (500 ppmv) reference standards.

---

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

| Chemical Formula | Degradation Products of CSK | Degradation Products of HFO |
|------------------|-----------------------------|-----------------------------|
|                     | CF₄ | C₂F₆ | C₃F₆ | C₅HF₂ | CH₂F₂ | Cis-C₅F₁₀ |
| t<sub>r</sub> (min) | 2.50 | 3.85 | 10.0 | 14.5 | 5.5 | 17.19 |
| Molecular Weight (g/mol) | 88 | 138 | 150 | 170 | 52 | 114 |
| GWP (100 years) | 7390 | 12200 | <5 | 2900 | 675 | 1 |
| Toxicity (L/C₅F₄ 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.
H₂O is analyzed because of its possible problem of generating degradation compounds and CO due to its toxicity.

### Table 7. Concentration of CO, H₂O, C₃F₆, and C₃HF₇ in the Samples Studied

| Samples          | CO (ppm) | H₂O (ppm) | C₃F₆ (ppm) | C₃HF₇ (ppm) |
|------------------|----------|-----------|------------|-------------|
| 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 C₃F₆ and C₃HF₇ were built from 0.01 to 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 C₃F₆ (≤ 0.04%), C₃HF₇ (≤ 0.4%), and a certain amount of CO (≤ 1%), H₂O (≤ 0.006%) have been found in the mixtures.

### Table 8. Variation of Response with the Concentration of C₃F₆ and C₃HF₇ by GC/MS

| Technique | Analyte | Linear Response |
|-----------|---------|-----------------|
| GC/MS     | C₃F₆   | y = 4E06x, r² = 0.9927 |
|           | C₃HF₇ | y = 8E06x, r² = 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 C₃F₆ (≤ 0.04%), C₃HF₇ (≤ 0.4%), and a certain amount of CO (≤ 1%), H₂O (≤ 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 CSK and the most abundant degradation compounds (C₃F₆ and C₃HF₇). 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 cm³ 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 C₃F₆ and C₃HF₇ contents in gas samples. C₃F₆ and C₃HF₇ concentrations were calculated by dividing their GC-FID chromatographic signal area by the chromatographic signal area of CSK, and the result was multiplied by the known concentration of CSK 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 CSK and HFO with synthetic air and CO₂ have been identified. CF₄ (tetrafluoromethane), C₂F₆ (hexafluoroethane), C₃F₆ (hexafluoropropylene), and C₃HF₇ (1,1,1,2,2,3,3-heptafluoropropane) are the degradation products from CSK, and CH₂F₂ (Difluoromethane) and trans-C₃H₂F₄ (1,3,3,3-Tetrafluoropropene) are the degradation products from HFO.

In this work, small quantities of weakly toxic C₃F₆ (≤ 0.04%), C₃HF₇ (≤ 0.4%), and a certain amount of CO (≤ 1%) and H₂O (≤ 0.006%) have been found.

It is possible that part of C₃HF₇ dehydrofluorinates to form C₃F₆. The presence of C₃HF₇ in samples of gas mixtures with CSK can be explained from a reaction of fluoroketone CSK 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...
adsorbing or absorbing the 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 SF6 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 ≥99.5% weight. Moisture content ≤50 ppm weight and nonvolatile residue ≤50 ppm weight. CSK was obtained from 3M (Minnesota, USA). Purity 99.5%. CO2 and synthetic air were supplied by Carburos Metalicos and Air Liquid (Madrid, Spain) and were used as dilution gases for preparing the calibration curves of different dielectric gases assayed. The decomposition products CO, C3F6, and C3HF7 were acquired as a mixture of 500 ppmv of each gas in He (CO-C3HF6-C3HF7-He) from Air Liquid (Madrid, Spain) to be used as a gas reference standard. Finally, an additional gas reference standard with 50 ppm weight and nonvolatile residue 50 ppm weight. C5K was obtained from 3M (Minnesota, USA). Purity 99.5% weight. CO2 and synthetic air were supplied by Carburos Metalicos and Air Liquid (Madrid, Spain). Degradation products are of permanent gases: H2,O, CO2, methane, air, CO, water, polar solvents, and sulfur compounds (H2S). HP-Molesieve columns, made of zeolite, are ideal for many applications, including routine air monitoring for the analysis of fixed and permanent gases: H2, O2, N2, CO, CH4, He, Ne, Ar, Kr, Xe, and SF6. 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⁻¹ to 75 °C; finally, the oven temperature was increased at a rate of 5 °C min⁻¹ 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](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](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 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 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 cm³ Tedlar bags, Vertex (Barcelona, Spain), to be analyzed on the Chromatographic separation in terms of resolution. The sensitivity and repeatability, along with an acceptable 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 (Minnetonka, USA).

Table 10. Gas Mixture Samples Analyzed

| MV switchgear | Gas Mixture          |
|---------------|----------------------|
| cubicle #1 (4 years at 30kV) | 20% C5K + CO₂ |
| cubicle #2 (1.5 years at 30kV) | 78% HFO + CO₂ |
| cubicle #3 (1.5 years at 30kV) | 10% C5K + synthetic air |
| cubicle #4 (1.5 years at 30kV) | 10% C5K + 3% HFO + synthetic air |

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 (Minnetonka, USA).

- **AUTHOR INFORMATION**

**Corresponding Author**

María Luz Alonso – Analytical Chemistry Department, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), 48940 Leioa, Bizkaia, Spain; orcid.org/0000-0002-2027-9411; Email: marialuz.alonso@ehu.eus

**Authors**

Rosa María Alonso – Analytical Chemistry Department, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), 48940 Leioa, Bizkaia, Spain

José Ignacio Lombrana – Chemical Engineering Department, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), 48940 Leioa, Bizkaia, Spain

Jesús Izcara – Ormaezabal Corporate Technology, 48340 Amorebieta-Etxano, Bizkaia, Spain

Josu Izagirre – Ormaezabal Corporate Technology, 48340 Amorebieta-Etxano, Bizkaia, Spain

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02512

**Funding**

This work was supported the Basque Country Government (project Elkartek KK-2017/00090).

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Authors thank 3M Company for interlaboratory assay.

**REFERENCES**

(1) https://www.ipcc.ch [accessed 1 May 2020].

(2) Tsai, W. The decomposition products of sulfur hexafluoride (SF6): reviews of environmental and health risk analysis. J. Fluorine Chem. 2007, 128, 1345–1352.

(3) Tatarinov, A. V.; Bilera, I. V.; Avtueva, S. V.; Shakhatov, V. A.; Solomakhin, P. V.; Maladen, R.; Prévé, C.; Piccoz, D. Dielectric barrier discharge processing of trans-CF₃CH=CHF and CF₃C(O)-CF(CF₃)₂, their mixtures with air, N₂, CO₂ and analysis of their decomposition products. Plasma Chem. Plasma Process. 2015, 35, 845–862.

(4) Seeger, M.; Smeets, R.; Yan, J.; Iod, H.; Claessens, M.; Dullini, E.; Falkingham, L.; Franck, C. M.; Gentils, F.; Hartmann, W.; Kieffel, Y.; Jia, S.; Jones, G.; Mantilla, J.; Pawar, S.; Rabie, M.; Robin-Jouan, P.; Schelleken, H.; Spencer, J.; Uchia, T.; Li, X.; Yanabu, S. Recent trends in development of high voltage circuit breakers with SF6 alternative gases. PPT 2017, 4, 8–12.

(5) Beroual, A.; Haddad, A. Recent Advances in the Quest for a New Insulation Gas with a Low Impact on the Environment to Replace Sulfur Hexafluoride (SF6) Gas in High-Voltage Power Network Applications. Energies 2017, 10, 1–20.

(6) https://pubchem.ncbi.nlm.nih.gov [accessed 1 March 2021].

(7) Wang, Y.; Gao, Z.; Wang, B.; Zhou, W.; Yu, P.; Luo, Y. Synthesis and Dielectric Properties of Trifluoromethanesulfonfluoride: An Alternative Gas to SF6. Ind. Eng. Chem. Res. 2019, 58, 21913–21920.

(8) Zhang, X.; Li, Y.; Chen, D.; Xiao, S.; Tian, S.; Tang, J.; Wang, D. Dissociative adsorption of environment-friendly insulating medium C3F7CN on Cu(111) and Al(111) surface: A theoretical evaluation. Appl. Surf. Sci. 2018, 434, 549–560.

(9) Preve, C.; Piccoz, D.; Maladen, R. Presented in part at 23rd International Conference on Electricity Distribution; Lyon: June, 2015.

(10) Safety data sheet of Solstice-1234ze, according to Regulation (EC)No.1907/2006. http://www.harpintl.com/downloads/pdf/msds/Solstice-1234ze-SDS-CLP.pdf [accessed 1 March 2021].
(11) Tatarinov, A. V.; Bilera, I. V.; Shakhatov, V. A.; Avtaeva, S. V.; Solomakhin, P. V.; Maladen, R.; Prévé, C.; Piccoz, D. Comparative Study of Degradation of trans-1,3,3,3- Trifluoropropene, 2,3,3,3- Tetrafluoropropene, Perfluoro-3-methylbutanone-2, and Sulfur Hexafluoride in Dielectric Barrier Discharge. High Energy Chem. 2016, 50, 64−70.

(12) Kessler, F.; Sarfert-Gast, W.; Ise, M.; Goll, F. Presented in part at the 20th International Symposium on High Voltage Engineering; Argentina, August 2017.

(13) Lutz, B.; Juhr, K.; Kuschel, M.; Glabitz, P. CIGRE Colloquium Study Committees, http://www.cigre.org, 2017

(14) Zhang, X.; Tian, S.; Xiao, S.; Deng, Z.; Tang, J. Insulation Strength and Decomposition Characteristics of a C6F12O and N2 Gas Mixture. Energies 2017, 10, 1170.

(15) Lokhat, D.; Ramjugernath, D.; Starzak, M. Simultaneous Separation of perfluorocarbons and Oxylfluorocarbons Using Capillary Gas Chromatography: Analysis of the Products of Hexafluoropropene Oxidation. J. Anal. Chem. 2014, 69, 98−103.

(16) Orue, I.; Gilbert, I.; Larrieta, J.; Sánchez, J.A. Presented in part at the CIRED 24th International conference on Electricity Distribution; Glasgow, June 2017.

(17) Barrios, S.; Gilbert, I.; Hurtado, A.; Mukroy, P.; Orue, I. Presented in Smargrinet; Croatia, April 2018.

(18) https://www.cdc.gov/nciost/index.htm. [accessed 1 March 2021].

(19) Pohanish, R.P. Sittig’s Handbook of Toxic and Hazardous Chemical Carcinogens; 6th ed. New York: Waltham; 2012.

(20) O’Neil, M.J. The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals; 15th ed.; Royal Society of Chemistry: Cambridge, 2013; 1−2708.

(21) Lewis, R.J. Hawley’s Condensed Chemical Dictionary; 15th ed.; John Wiley & Sons: New York,2007; 1−4000.

(22) U.S. National Archives and Records Administration’s Electronic Code of Federal Regulations. http://www.ecfr.gov. [accessed 1 March 2021].

(23) Bretherick, L. Handbook of Reactive Chemical Hazards; 4th ed.; Butterworth-Heinemann Ltd.: Boston, 1990,1−2058.

(24) https://unfccc.int. [accessed 1 March 2021].

(25) Gong, M.; Zhao, Y.; Dong, X. Measurements of isothermal (vapor + liquid) equilibrium for the (propane + cis-1,3,3,3-tetrafluoropropene) system at temperatures from (253.150 to 293.150) K. The Journal of Chemical Thermodynamics 2016, 103, 349−354.

(26) Liang, Y.; Wang, F.; Sun, Q.; Zhai, Y. Molecular structural and electrical properties of trans-1,3,3,3-tetrafluoropropene and 2,3,3,3-tetrafluoropropene under external electric fields. Comput. Theor. Chem. 2017, 1120, 79−83.

(27) Wang, Y.; Huang, D.; Liu, J.; Zhang, Y.; Zeng, L. Alternative Environmentally Friendly Insulating Gases for SF6. Processes 2019, 7, 216−230.

(28) Zhang, X.; Li, Y.; Tian, S.; Xiao, S.; Chen, D.; Tang, J.; Zhuo, R. Decomposition mechanism of the CS-PFK/CO2 gas mixture as an alternative gas for SF6. Chem. Eng. J. 2018, 336, 38−46.

(29) Zhang, X.; Li, Y.; Xiao, S.; Tang, J.; Tian, S.; Deng, Z. Decomposition Mechanism of CSF100: An Environmentally Friendly Insulation Medium. Environ. Sci. Technol. 2017, 51, 10127.

(30) Zhang, Y.; Zhang, X.; Li, Y.; Li, Y.; Chen, Q.; Zhang, G.; Xiao, S.; Tang, J. AC breakdown and decomposition characteristics of environmental friendly gas CSF100/Air and CSF100/N2. IEEE Access 2019, 7, 73954−73960.

(31) https://www.epa.gov⟩iris. [accessed 1 March 2021].

(32) https://www.iarc.fr. [accessed 1 March 2021].

(33) https://ntp.niehs.nih.gov⟩roc14. [accessed 1 March 2021].

(34) Boethling, R. S.; Meylan, P. H.; Meylan, W.; Stiteler, W.; Beauman, J.; Tirdo, N. Group contribution method for predicting probability and rate of aerobic biodegradation. Environ. Sci. Technol. 1994, 28, 459−465.