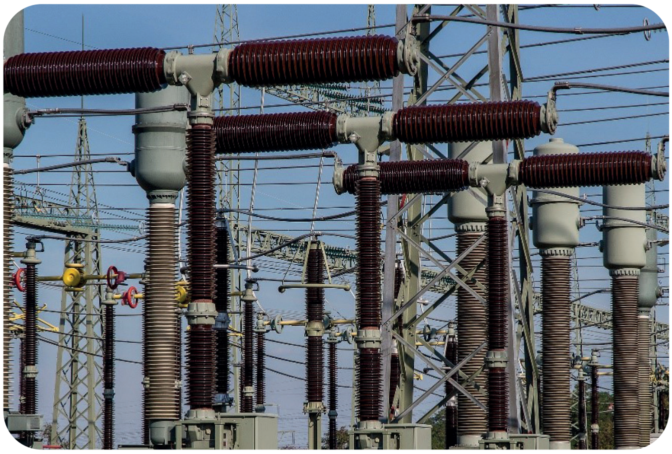
Application Note AN M166



Quantitative Analysis of the Novel Dielectric Gas g^3 with the FTIR Gas Analyzer MATRIX-MG5

Introduction

Present-day transmission and distribution networks have in common that they use SF_6 as insulating gas due to its arc quenching and dielectric properties [1]. Being non-flammable and non-toxic, SF_6 features a generally inert nature which makes it even more suitable to be used for high voltage switching applications. As is often the case, these unique characteristics bring along a drawback of SF_6 which is not to be scoffed at, especially in the era of climate debates: With a global warming potential (GWP) which is 23,500 higher than the one of CO_2, SF_6 is known as the most effective greenhouse gas [2]. For this reason, more than ever, alternative insulating gases are called for.

One promising replacement gas is g^3 (green gas for grid), a gas mixture developed by GE Grid Solutions in association with 3M™ [3]. g^3 has by two orders of magnitude less impact on global warming and, at the same time, a dielectric performance comparable to SF_6 (see Table 1). Furthermore, g^3 is non-flammable, has a sufficiently high vapor pressure and low toxicity (LC_{50_4h} = 1.6 mol% for male mice), even after typical release scenarios, i.e. no additional safety labels are required compared to SF_6 [4]. g^3 is a gas mixture consisting of the fluoronitrile heptafluoro-iso-butyronitrile $(CF_3)_2$-CF-CN, a.k.a. 3M™ Novec™ 4710 dielectric fluid, and CO_2. Typically, g^3 contains 4-6% Novec™ 4710, depending on the required temperature and pressure. CO_2 fulfills at least two functions in the mixture: It keeps the GWP low and at the same time it reduces the boiling point of Novec™ 4710 significantly, enabling the usage of the mixture gas g^3 even at low temperatures.

Keywords	Instrumentation and Software
High-voltage applications	MATRIX-MG5
Impurities in dielectric gases	OPUS GA
ppm detection limits	VERTEX 80


Image 1: MATRIX-MG5 gas analyzer with 5 m gas cell.

Gas	P_{min}[MPa]	T_{min}[°C]	GWP	D.S.
SF_6	0.43...0.6	-41...-31	23,500	0.86...1
g^3	0.67...0.82	-25...-10	327...690	0.87...0.96

Gas	LC_{50} [ppmv]	SLF perform. comp. to SF_6	Dielectric R.S	D.S.
SF_6	-	1	1	0.86...1
g^3	>10^5	-0.83...(1)	close to 1	0.87...0.96

Table 1: Properties and switching performance of SF_6 and g^3 in high-voltage applications [2].
Abbreviations: p_{min}/T_{min}=minimal operating pressure/temperature, GWP=global warming potential comp. to CO_2, D.S.=dielectic strength compared to SF_6, LC_{50}=Lethal concentration that kills 50% of the test animals, SLF=short line fault, R.S.=recovery speed.

Monitoring of the composition of g^3 is of interest in many respects: In the event of a voltage breakdown due to over-voltage, the resulting “arced” g^3 gas sample is known to have a reduced amount of CO_2 and Novec™ 4710, i.e. the insulating property decays [1,2,5]. At the same time other compounds like CO and fluorinated compounds emerge in the gas mixture, leading to an increasing toxicity which must be controlled. An analysis of the gas composition is advisable to check for both the insulating efficacy and health safety.

The underlying study shows that the FTIR gas analyzer MATRIX-MG5 with its outstanding sensitivity is perfectly suited to analyze a g^3 gas sample quantitatively. With its compact, rugged design, it serves as a robust analytical solution even in the presence of vibrations. The calibration-free gas analysis software OPUS GA allows for a reliable quantification of the contaminants, while compensating for the carrier and other interfering gases, such as CO_2 and Novec™ 4710.

To verify the analytical method quantitatively, two measurements were conducted:

- Analysis of the gas composition of a pure g^3 gas sample, purchased from 3M™
- Analysis of the gas composition of an arced g^3 gas sample

As a basis for the gas analytical instrumentation, a reference spectrum of Novec™ 4710 was first recorded with the VERTEX 80 FTIR spectrometer. The barometric calibration provides a relative accuracy better than 2%. This reference spectrum was then used to create an analysis method with the OPUS GA gas analysis software for a real-time analysis of the g^3 gas sample.

Experimental procedure

The quantitative analysis of the gas samples was performed using the FTIR gas analyzer MATRIX-MG5 spectrometer with a gas cell with 5 m optical path length and a liquid nitrogen cooled MCT detector. All measurements were performed at room temperature using a spectral resolution of 1cm^{-1} by accumulating 80 scans, leading to an effective measurement time of about 11 s per spectrum.

In order to quantify also the concentration of gas compounds which only show spectral signatures in the spectral range where total absorption occurs, a dilution series was performed for both, the pure and the impure g^3 sample.

Via a T-connector and valves, the gas cell was connected to a nitrogen supply line and the sample bag containing the g^3 gas sample.

First, the gas cell was evacuated, then the valve was opened so that the gas sample could enter the gas cell. Then the valve to the gas sample bag was closed, the sample pressure p_i was reduced in a controlled manner and diluted with pure nitrogen to about 1000 mbar total pressure (p_{tot}). After the dilution, the valves were closed. This procedure was repeated for each dilution of the dilution series illustrated in Figure 1.

For each filling, the temperature T, the partial sample pressure p_i and the total pressure p_{tot} were notated. This allowed to measure the serial dilution quantitatively, in order to evaluate the volume mixing ratio versus the dilution p_i/p_{tot} of the gas sample. During the complete filling procedure, a real-time analysis was conducted with the gas analysis software OPUS GA.

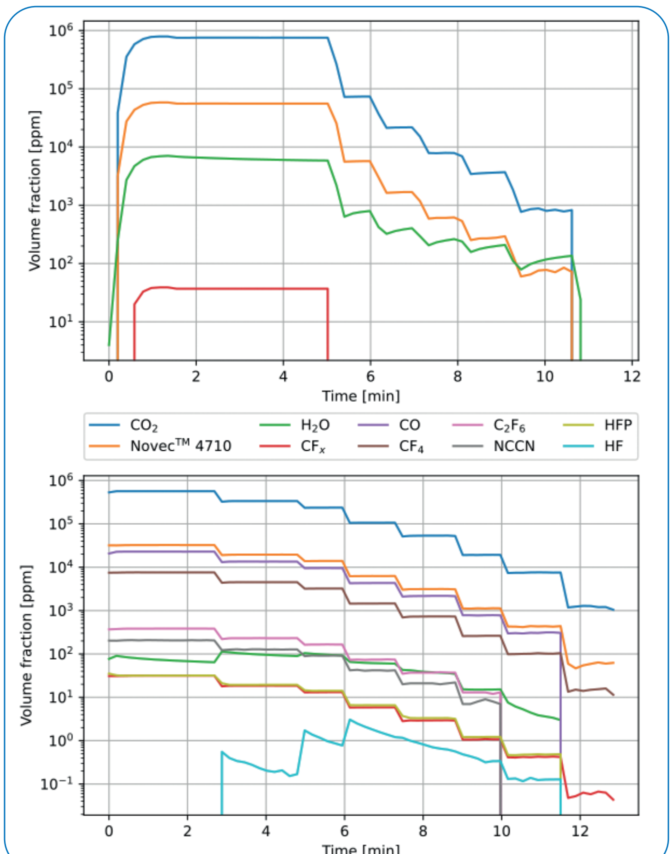


Figure 1: Measured volume fractions of gas compounds of the pure (top) and impure (bottom) g^3 sample during serial dilution. For each measured concentration level, the gas cell was refilled with a new gas sample. The strongly fluctuating measurement results during sample preparation (pumping, filling) are not displayed for reasons of clarity.

The exact volume mixing ratios of the gas compounds were finally determined from the slope of the line of best linear fit in the plot of volume mixing ratio versus the dilution of the g^3 gas sample.

Measurement results

The evaluation of the pure g^3 sample from 3M™ shows a composition of about 92% CO_2 and 7% Novec™ 4710. The residual humidity (approx. 25% relative humidity at 25°C) is most likely caused by storing or filling the samples. Also, a volume fraction of CF_x in the order of tens of ppm could be clearly identified via OPUS GA, which could be explained by the rather inert residual reactivity of Novec™ 4710 with CO_2. Figure 1, top, illustrates the time course of the full dilution series.

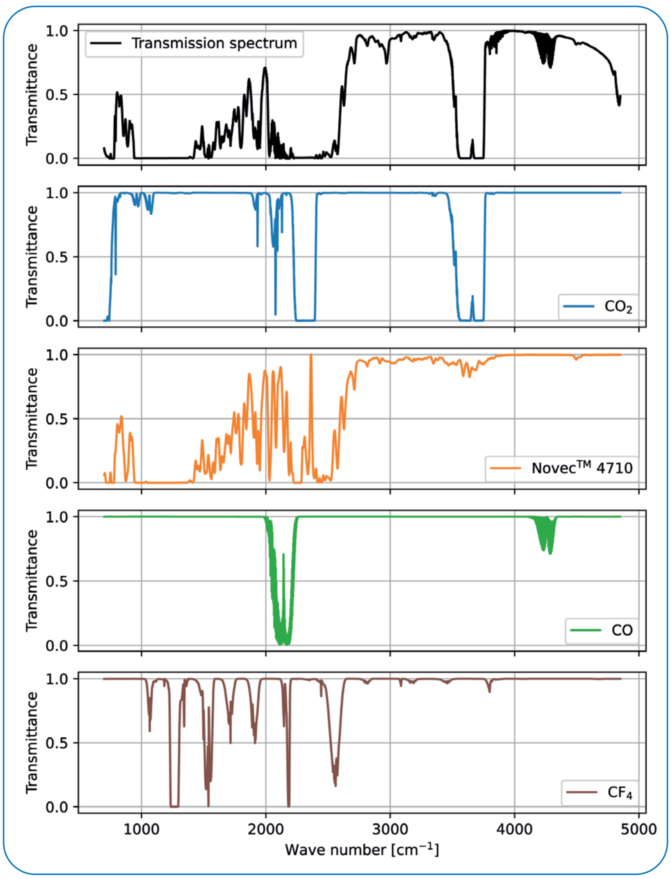


Figure 2: IR transmissions of the diluted g^3 mixture (65% in N_2, top) contaminated by decomposition products, the main components CO_2 and Novec™ 4710 as well as the pre-dominant impurities CO and CF4. The decomposition product carbon monoxide (CO) can be directly seen due to the spectral lines in the fundamental band at 2143 cm^{-1} and the overtone band at 4260 cm^{-1}.

For the impure, i.e. arced, g^3 sample, the sample moisture appears to be significantly reduced by reaction with unstable contaminants, such as carbonyl fluoride. Table 2 lists the measured impurities that are mainly formed by the thermal and electrochemical decomposition of the g^3 insulating gas [1]. The measured spectrum of the impure g^3 sample and its decomposition into its principal gas compounds is visualized in Figure 2.

As expected, in the arced g^3 sample the proportion of CO_2 in the used g^3 (-2.6%) and Novec™ 4710 (-1.6%) decreased (see Figure 1, bottom, and 3). At the same time, a large fraction of CO was formed (3.6 vol%) along with a total of about 1.4 vol% other components, of which CF_4 (tetrafluoromethane, 1.2 vol%) contributed by far the largest proportion of the C_xF_y. Hexafluoroethane is detectable at 0.06 vol%. Highly homologous fluorinated alkanes were not found in the mixture however or were present below the detection limit (volume fractions far below 1 ppm).

Despite their small volume fraction, even hydrogen cyanide (HCN), cyanogen (CN-CN), hydrogen fluoride (HF) and hexafluoropropylene (HFP) could be identified very clearly (see Table 2). However, HF could not be analyzed in a pristine manner because it turned out to stick to the surface of the sample bag and gas cell due to its reactivity and polarity. After filling the gas cell, the HF volume fraction decreased distinctly over time (see Figure 1, bottom). The dilution series from low to high dilution shows no HF in the lowest dilution (66% in N_2, see Figure 4). With increasing sample dilution an increasing mean HF volume fraction is measured up to a g^3 dilution of 10 vol%. For a g^3 volume fraction below 10 vol%, the HF volume fraction drops to zero. For a reliable HF analysis, continuous flow sampling until an equilibrium fraction is reached, combined with a heated gas cell, would be the right choice to hamper the reactivity of HF with the bag and gas cell surface.

The group of fluorinated alkyl-CN ($C_xH_yF_z$-CN) could not be specifically identified due to the lack of reference spectra. However, 2 to 4 unknown components in the FTIR spectrum are unspecifically detectable by the spectral signature of the IR-active functional groups C-F and C-H. Based on the typical band strengths of connections with the same groups, a rough limitation of the volume fractions <100 ppm can be estimated. These groups could belong to the $C_xH_yF_z$-CN.

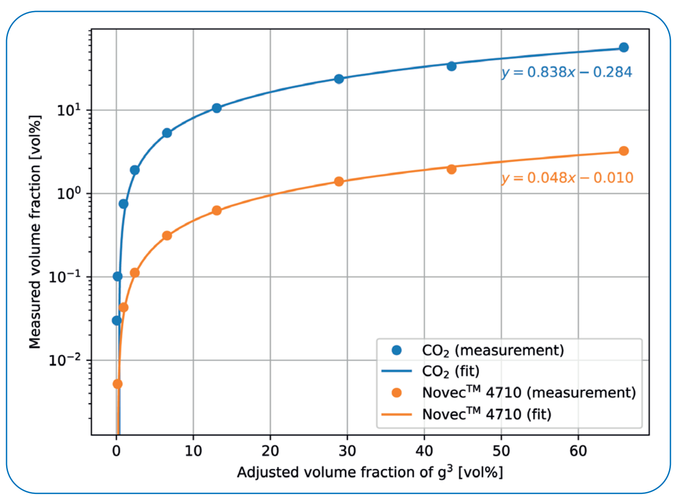


Figure 3: Evaluation of the impure g^3 sample by analyzing the serial dilution versus the measured volume fractions of CO_2 (blue) and Novec™ 4710 (orange).

Carbonyl fluoride was clearly not found in the impure g³ mixture. This is not surprising because, in the presence of moisture, the substance quickly decomposes to hydrogen fluoride and carbon dioxide according to $COF_2 + H_2O \rightarrow CO_2 + 2HF$. The decreased sample moisture (0.05 vol%) of the contaminated sample compared to the pure sample (0.8 vol%) could be an indicator for the decomposition of such reactive fluorinated components.

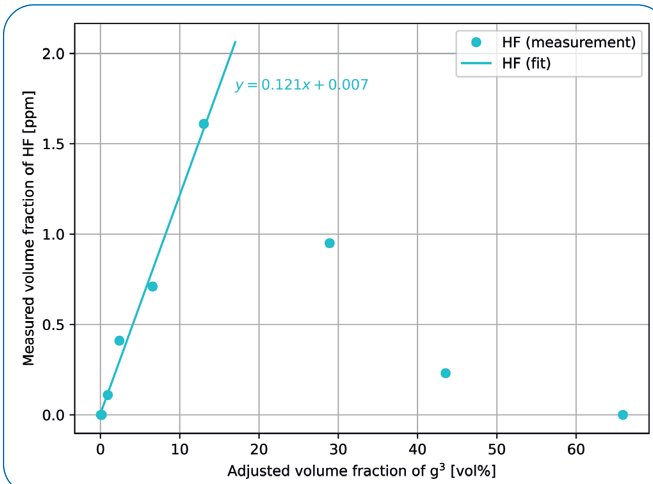


Figure 4: Measured HF volume fraction in the dilution series of g³. The dilution time course is from right to left. The dashed line shows the best linear fit to the last five data points of the serial dilution. For every measuring point, the gas cell was filled with a new gas sample.

Summary

The FTIR gas analyzer MATRIX-MG5 was used to quantify the constituents of the dielectric gas g³, before and after applying a breakdown voltage. The gas analysis software OPUS GA allowed a reliable quantification of the gas composition, even in spite of total absorption of the IR light by the g³ gas over a large spectral range. Dilution series of the g³ gas were evaluated to determine the exact volume mixing ratios of its constituents.

		Volume Fraction [vol%]	
Compound	**CAS Number**	**Pure g³**	**Impure g³**
CO_2	124-38-9	92.4	89.8
Novec™ 4710	42532-60-5	6.8	5.2
CO	630-08-0		3.6
CF_4	75-73-0		1.2
		Volume Fraction [ppm]	
		Pure g³	**Impure g³**
H_2O	7732-18-5	7522	490
C_2F_6	76-16-4		614
NCCN	460-19-5		332
HFP	116-15-4		51
SF_6	2551-62-4		36
CH_x			32
HF	7664-39-3		13
HCN	74-90-0		5.2
H-C-unknown			5.0
CF_x		45	5.0

Table 2: Analysis results for the measured g³ samples. The absolute analysis values were derived from the gradients in the dilution/volume fraction diagrams and scaled to 100% (by a factor of 1.07) to yield the relative composition of the sample.

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