ONE VISION. ZERO EMISSIONS.



WHITE PAPER

Measuring gas quality and sustainable reconditioning and reuse of Alternative Gases Part 4

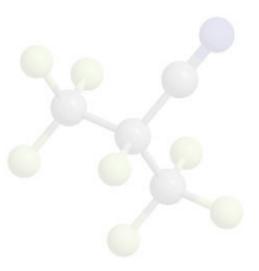
Authors Dr Sebastian Glomb Martin Göppel Peter Pilzecker

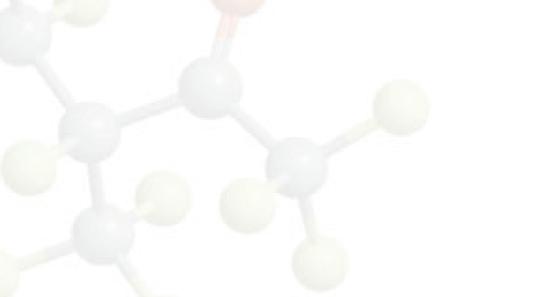


Table of contents

1

1. Introduction	2
2. Measuring gas quality of Alternative Gases	3—5
3. Detecting Alternative Gases	5
4. Sustainable reconditioning and reuse of Alternative Gases	6—8
5. Final thoughts	8
6. References	8





1. Introduction

The final part of the guide on Alternative Gases will cover fundamental aspects concerning measurement of the Alternative Gases' constituents and provides an overview over the elementary differences in terms of sensors when contrasted with SF_6 measurement. The paper will outline existing monitoring systems such as leak testers and ambient air monitors and illustrate the possibilities available for sustainable reconditioning and reuse of Alternative Gases.

Gas quality is measured, or the gas and gas mixtures contained in operating media are checked for, when a system is first filled or put into commission, when gas is recovered, when a system undergoes maintenance or at the end of its service life (decommissioning). The primary concern here is to establish whether the gas mixture will be put back into use, reconditioned or disposed of. Applicable standards may serve as aids in reaching a decision, otherwise we will need to refer back to the manufacturer's specifications. Much like a human's blood count, the gas's quality will shine a light on the system's past. Incorrect handling of the gas, poor evacuation and discharges can thus still be detected in retrospect.

Unlike SF_6 applications, with SF_6 acting as the sole insulating component in gas-charged equipment or as arc quencher in switchgear, alternative gases often comprise multiple constituents (see Guide 1). To function properly, they require precisely tuned mixing ratios and accurate measurement of the various constituents' concentration levels.

2. Measuring gas quality of Alternative Gases

In SF₆ applications, measured values are first and foremost SF₆ purity (percentage share of SF₆ allows indirect inference of air and CF₄ shares), the gas's moisture content and its decomposition product load, indicated by the SO₂ concentration. Conducting measurements on equipment filled with SF₆ is described in detail in the "SF₆ Measurement Guide¹". The guide can also be applied for the most part when measuring Alternative Gases as the measurement methods and procedures are the same.

The properties of alternative gas mixtures depend on the respective constituents used. The accuracy to which each constituent is measured will be prioritised according to the purpose the respective gas constituent is fulfilling. Utmost priority is afforded those constituents acting as insulation and arc quencher in switchgear. Thresholds for mixing ratios and measurement accuracy are presently still provided by the various switchgears' manufacturers. The available measuring devices' designs reflect their specifications (Figure 1). The latest technology for measuring gas quality uses a fully enclosed system and produces zero emissions.

Concentrations of insulating gas and by-products are indicated as mole fraction in mol% or ppm. Mole fraction is equivalent to the <u>ideal</u> volume fraction, but unlike the <u>real</u> volume fraction (vol%, ppm_v) is <u>not</u> affected by temperature or pressure. The certified testing gases required



Figure 1: MultiAnalyser for measuring concentration of C4-FN or C5-FK, oxygen (O_2) , moisture (using electr. dew point sensor), carbon dioxide (CO₂) and carbon monoxide fraction (CO).

for calibrating the sensors are produced gravimetrically, which means that separate constituents of the gas mixtures are weighed precisely before they are added. This makes the testing gases equally **independent** to temperature and pressure and means they are directly traceable to the international standard of mass.

The constituents measured in the Alternative Gases may be the insulating gas itself (C4-FN is equivalent to 3M[™] Novec[™] 4710, C5-FK is equivalent to 3M[™] Novec[™] 5110), the carrier gas (CO_2) or other typical constituents (oxygen; O₂). Consistent quality parameters that are measured are, as is the case for ${\rm SF}_{\!_{\rm f}},$ moisture (H__0) and indicators for the fraction of decomposition products, such as SO₂). Indicators considered typical for C4-FN/C5-FK applications are the fraction of carbon monoxide (CO) and, in applications with Synthetic Air, the proportion of nitrogen oxides ($NO_{v} = NO$ and NO_{2}). Determining the moisture requires consideration of the carrier gas used as the moisture sensors used need to be calibrated accordingly. The currently common sensor systems (e.g. electrochemical or optical) are not capable of supplying on-site measurement of the nitrogen fraction (N_2) , for example for applications with Synthetic Air. One of the feasible laboratory measurement methods is gas chromatography, in which a gas mixture is broken down into its constituents using a capillary column so that nitrogen can then be quantified separately.

The technology employed in the various sensors, the measuring range and accuracy differ considerably from those of SF₆ measuring devices (Figure 2). The investigated C4-FN/C5-FK mole fraction will be a lot smaller ($\leq 15 \text{ mol}\%$), the concentration range thus requiring sensors designed specifically to match. One feasible method is using non-dispersive infrared measurement (ND-IR). ND-IR sensors measure the signal strength of a specific molecular oscillation stimulated by the absorption of a photonic wavelength specific to the molecule. By choosing the corresponding oscillation, the sensors target molecules selectively. As a consequence, other gases do <u>not</u> affect the measurement result. Also, compared with mea-

suring SF₆ fraction ratios at the speed of sound, ND-IR sensors supply greater accuracy (C4-FN/C5-FK: ±0.1 %, SF₆: ±0.5 %). Another point of note is that, unlike when measuring SF₆ purity (single-component gas), measuring fractions in gas mixtures comprising multiple constituents may supply deviating measurement results, for example because additional ingress of ambient air have caused shifts in the filling ratio. When pursuing accurate measurement results, it thus makes sense to determine to the concentration of each constituent separately.

There are two main methods for determining moisture in Alternative Gases, which always depends on the Alternative Gas itself. Moisture in Synthetic Air can be determined either physically by measuring the dew/frost point or by performing capacitive moisture measurement. Mixtures with C4-FN/C5-FK require use of a capacitive moisture sensor. Because of the very low boiling points of C4-FN and C5-FK. As a consequence, cooling during measurement with a dew point meter may cause them to condense before the moisture, thus producing false measurement results.

Oxygen and carbon monoxide fractions as well as nitrogen oxides (NO and NO_2) in Synthetic Air applications can be measured using electrochemical sensors. Presence of the target gas in the gas mixture triggers an electrochemical reaction inside these sensors, the reaction producing a

current or voltage proportional with the measured concentration. These sensors, too, are tailored highly specifically to the constituents they measure.

Their stability or service life is similar to those in SF_6 devices, so they should likewise be recalibrated or replaced once every two years. The devices themselves are designed and used much like SF_6 analysers. They thus offer familiar features like zero-emissions measuring and pump-back function. To provide an example, here are technical specifications for available sensors for C4-FN/ C5-FK applications:

So far, this paper has presented applications suitable for determining gas quality by means of on-site measurement. Evidently, just as with SF_6 applications, taking gas samples will allow full analysis in a professionally equipped laboratory, including determining all decomposition products and other gases like nitrogen by means of gas chromatography or FT-IR spectrometers.

	Mol% 3M™ Novec™ 4710	Mol% 3M™ Novec™ 5110	Moisture	Mol% oxygen (O ₂)	Mol% carbon dioxide (CO ₂)	Concentration carbon monoxide (CO)
Measuring principle/sensor	Non-dispersive infrared sensor (NDIR)	Non-dispersive infrared sensor (NDIR)	Electronic dew point measurement (capacitive)	Electrochemical reaction	Non-dispersive infrared sensor (NDIR)	Electrochemical reaction
Measuring range	0 — 10 mol%	0 – 15 mol%	-60 °C to +20 °C	0 – 25 mol%	0 — 100 mol%	0 – 500 ppm
Measuring accuracy	$\leq \pm 0.1 \text{ mol}\% \text{ (at } < 7\%)$ $\leq \pm 0.2 \text{ mol}\% \text{ (at } \geq 7\%)$	$\leq \pm 0.1 \text{ mol}\% \text{ (at } < 7\%)$ $\leq \pm 0.2 \text{ mol}\% \text{ (at } \geq 7\%)$	$\leq \pm 2^{\circ}$ C (at > -40°C) $\leq \pm 3^{\circ}$ C (at < -40°C)	≤ ±0.2% mol%	$\leq \pm 2 \text{ mol}\%$	±2% of measuring range

Figure 2: Technical data and measuring principle of sensors for analysing alternative gases.

3. Detecting Alternative Gases

Besides directly determining gas quality, equipment filled with C4-FN or C5-FK mixtures can also be checked for leaks. Suitable leak detectors localise leaks and quantify leak volumes. To prevent cross-sensitivity when measuring, it is best to use sensors focused on detecting the gas's fluorine constituent by means of non-dispersive infrared spectroscopy. Devices of this kind are capable of detecting C4-FN and C5-FK leaks at rates down to 3 g per year. When quantifying C4-FN or C5-FK, it should also be noted that, unlike SF₆, they do not occur as a pure substance in the gas mixture, but are instead present as a fraction < 15 mol%. When measuring leak rates, this results in a reduction by about factor 10 compared with SF₆ applications. For detecting leaks in synthetic air applications, methods using C0₂ or ozone (0₃) are examined. In closed indoor areas housing systems or tanks filled with C4-FN or C5-FK, it makes sense to install ambient air monitors that alert to dangerous concentrations caused by gas leaks even before anyone enters the room. Such monitors can also use NDIR sensors to directly measure the C4-FN or C5-FK fluorine fraction in the ambient air. Ideally, the ambient air monitor – acting as it would purely as a warning system **against harm to personnel** – can be equipped with additional sensors to alert to raised SF₆ levels, harmful decomposition products or lack of oxygen.

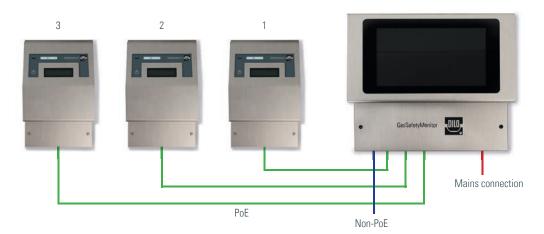


Figure 3: Example of network layout with different GasSafetySensors (left; 1-3) for measuring and a GasSafetyMonitor (right) for displaying.

4. Sustainable reconditioning and reuse of Aternative Gases

This final section discusses the concept of sustainable reconditioning and reuse of alternative gases after they have been used in switchgear.

Because SF_6 has such a high global warming potential, a whole range of international standards exist that specify minimum requirements for quality during operations and for handling disposal of the gases and gas mixtures used in switchgear. The broad variety of different mixtures and mixing ratios means that the necessary minimum gas quality and technical requirements can only be complied with throughout by noting the manufacturers' specifications.

At times when using Alternative Gases, after purification and drying the gas on site, reusing them may no longer be feasible or the required mixing ratio may have changed (<u>Guide 2</u>). If this is the case, there is still an alternative to disposing of them by incineration. Just like SF₆, reconditioning and recovery may be possible (for example by means of separating the fluorine constituents). Despite mixtures having an arithmetically lower GWP, especially in the case of C4-FN, gas mixtures with C4-FN and C5-FK should not be intentionally emitted into the atmosphere. Discharges during operations may produce toxic or environmentally harmful by-products, or both.

Specially designed, stationary reconditioning plants for recovering C4-FN and C5-FK already exist today. The complexity of the purification process does, however, preclude direct reconditioning on site. Reusing C4-FN or

C5-FK by adding fresh gas to the production process, a practice commonly employed for SF_6 (Solvay, "The SF_6 -ReUse-Process"²), technologically not feasible.

Unlike SF₆, the challenge in reconditioning Alternative Gases with C4-FN or C5-FK does not lie in separating the lion's share of constituents (typically CO_2/N_2) from the by-products. Instead, it is the smaller mole fraction (C4-FN/C5-FK) that is reconditioned. This makes reconditioning viable both ecologically and economically only if there is a sufficiently high proportion of C4-FN/C5-FK in comparison with any decomposition products and the separating process's recovery efficiency is high (> 95 %). After reconditioning, the gas is available for use in new mixtures, which can even have different mixing ratios or use different carrier gases than the original mixtures (Figure 4).

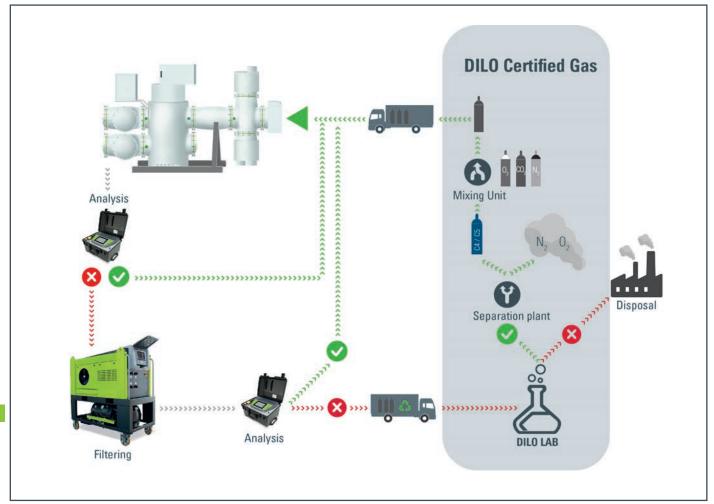


Figure 4: Closed cycle of analysis, reconditioning and reuse of Alternative Gases.

Reconditioning the remaining gases (CO_2, N_2, O_2) is not cost-effective. To prevent toxic or environmentally harmful by-products in the remaining gas, the relevant by-products need to be filtered out further and gas analysis under laboratory conditions is necessary. The remaining gas, now rendered harmless, can then be released into the atmosphere or disposed of appropriately.

When considering whether to perform reconditioning, ecological sustainability should be taken into account as much as cost factors. In terms of profitability, lower costs and rapid availability of mixtures with reconditioned gas present powerful arguments, as do country-specific aspects (availability of C4-FN/C5-FK, tax on new gas etc.). Ecological considerations, however, need to take into account the carbon footprint of the overall process as a whole. Positive factors of note in this respect are

that reconditioning consumes less power than disposal by incineration and that it saves resources because reusing the existing gas eliminates the need to synthesise C_4 or C_5 using new materials.

Other factors that are often neglected, but which impact the total carbon balance all the same, are the additional CO_2 emissions produced by transporting gas handling service carts between facilities, transport gas to the reconditioning plant, the energy expended for separation and the emissions produced in connection with building and maintaining the reconditioning plant. This means that the environmental impact caused by added energy expenditure for material transport and subsequent reconditioning or incineration needs to be considered very carefully where quantities are small. Transporting and reconditioning the separate constituents of synthetic air at external sites for recovery are not economically viable because nitrogen, oxygen and even carbon dioxide are comparatively cheap, are widely available and quickly obtained. The previous sections of this guide on Alternative Gases looked at the technical options for determining gas quality in gas enclosures and for monitoring ambient indoor air and detecting leaks, and presented details on the various measuring methods required. Aspects concerning sustainable reconditioning of C4-FN and C5-FK have also been explained, as has the existing option for reusing the gases in a closedloop cycle.

5. Final thoughts

The guides on Alternative Gases are intended to reduce uncertainty among potential users when considering switching to or handling Alternative Gases. The aim was to illustrate that gas handling solutions for the various Alternative Gases available today are already technologically proven and just as diverse as the range of alternative gases. At DILO, experience gained over more than fifty years of handling SF₆ gas has been incorporated into technical engineering, allowing us to rapidly expand our comprehensive range of service carts, measuring devices and services to also cover Alternative Gases. Handling Alternative Gases in some aspects appears more complicated and intricate, but remains similar to the methods for handling SF_6 that have emerged over the past fifty years. To this day, even the latter field is still undergoing technological innovation and optimisation, and accordingly the field of Alternative Gases offers potential for continuous improvement, too. DILO is keen to remain the reliable partner and world leader to act as your guide in the field for the next fifty years as well. As we always say:

ONE VISION. ZERO EMISSIONS.

The authors and all of the team at DILO look forward to hearing your questions and thoughts.

6. References

(1) CIGRÉ Technical Brochure No 723, 2018, SF₆ Measurement Guide.

(2) Solvay. The SF6-ReUse-Process: A contribution on the sustainability of SF₆.

ONE VISION. ZERO EMISSIONS.



SF ₆ GAS	ALTERNATIVE	INDUSTRIAL	HIGH PRESSURE
	GASES	GAS EQUIPMENT	PRODUCTS
DILO	AFTER SALES	TRAINING &	
CERTIFIED GAS	SERVICES	CERTIFICATION	

DILO Armaturen und Anlagen GmbH Frundsbergstrasse 36 D-87727 Babenhausen

(■ +49 (0) 83 33 3 02-302
(■ +49 (0) 83 33 3 02-302
(■ info@dilo-gmbh.com

