Version from August 25th, 2021 (Christian Franck)
Updated August 22th, 2022 (Michael Walter)
Update: 29.08.22 (Karsten Juhre)
Updated August 29th, 2022 (Michael Walter)

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Electric performance of new non-SF_6 gases and gas mixtures for gas-insulated systems

Presented by Karsten Juhre & Michael Walter
on behalf of WG D1.67 (convenor: Christian Franck)

Paris – 1.9.2022

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Working Group Scope

- Describe methods for identifying new insulating gases and gas mixtures.

- Investigate and summarize the dielectric properties and
- the practical insulation performance

of new non-SF_6 insulating gases and gas mixtures for gas-insulated systems.

[Terms of Reference, 18/08/2016]

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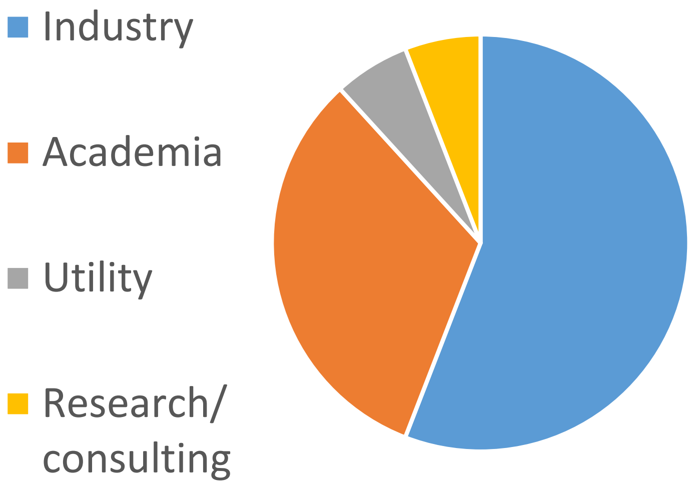

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Final Brochure - Table of Content

1. Executive summary
2. Introduction
3. Definitions, abbreviations and symbols
4. Description of methods to find new gases
5. Methods to characterize gases
6. Practical insulation performance
7. Definition of protocol and measurement guidelines for D1.67 round-robin test series
8. Summary of know-how on gases and gas mixtures
9. Results of round-robin electric test campaign
10. Results of round-robin gas analysis campaign
11. Summary and Conclusions

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Part A:
State-of-the-Art Summaries

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Part B:
Newly proposed test methods and procedures

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Part C:
Electrical Insulation Strength
of novel gas mixtures

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Part D:
Gas Mixture Analysis

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Part A

State-of-the-Art Summaries

[Status of 2019]

Typical SF_6 use conditions in MV and HV electrical equipment

	Type	Voltage range	Typical operating pressure of SF_6 (relative)	temperature range	Mass of SF_6 (order of magnitude)
MV	Ring main unit (RMU) / GIS	3.6-52 kV	Mainly 30 kPa, up to 250 kPa for the highest voltage range	-25 to 40 °C (indoor)	~1 kg
	Load break switches	3.6-52 kV	30 kPa	-25 to 40 °C (indoor)	~0.1 kg
	Circuit breaker	3.6-52 kV	250 - 500 kPa	-25 to 40 °C	~0.2 kg
	Auto-recloser	3.6-52 kV	30 kPa	-40 to 50 °C (outdoor)	~0.4 kg
HV	Gas-insulated switchgear	72.5 - 1200 kV	400 - 650 kPa	-30 (-50 °C with heating) to 40°C	30 - >1200 kg
	Circuit breakers (Live tank and Dead tank)	72.5 - 1200 kV	400 - 650 kPa	-30 to 40 °C	2 - >400 kg, various designs
	Gas-insulated lines	115 - 1200 kV	350 - 900 kPa at 20 °C (depending on voltage level and gas mixture)	-25 to 40 °C	5 - 30 kg/m, depending on voltage level
Mixtures with SF_6:					
SF_6/N_2	Circuit Breakers	72.5 - 735 kV	325 - 890 kPa	-50 to 40 °C	36-80 Vol% SF_6 3 kg to 73 kg
	Gas-insulated lines	230 - 550 kV	340 - 930 kPa	-30 to 40 °C	20-60 Vol% SF_6 3 - 6 kg/m
SF_6/CF_4	Circuit breakers	72.5 - 735 kV	600 - 900 kPa	-60 to 40 °C	25-52 Vol% SF_6 1 - 83 kg

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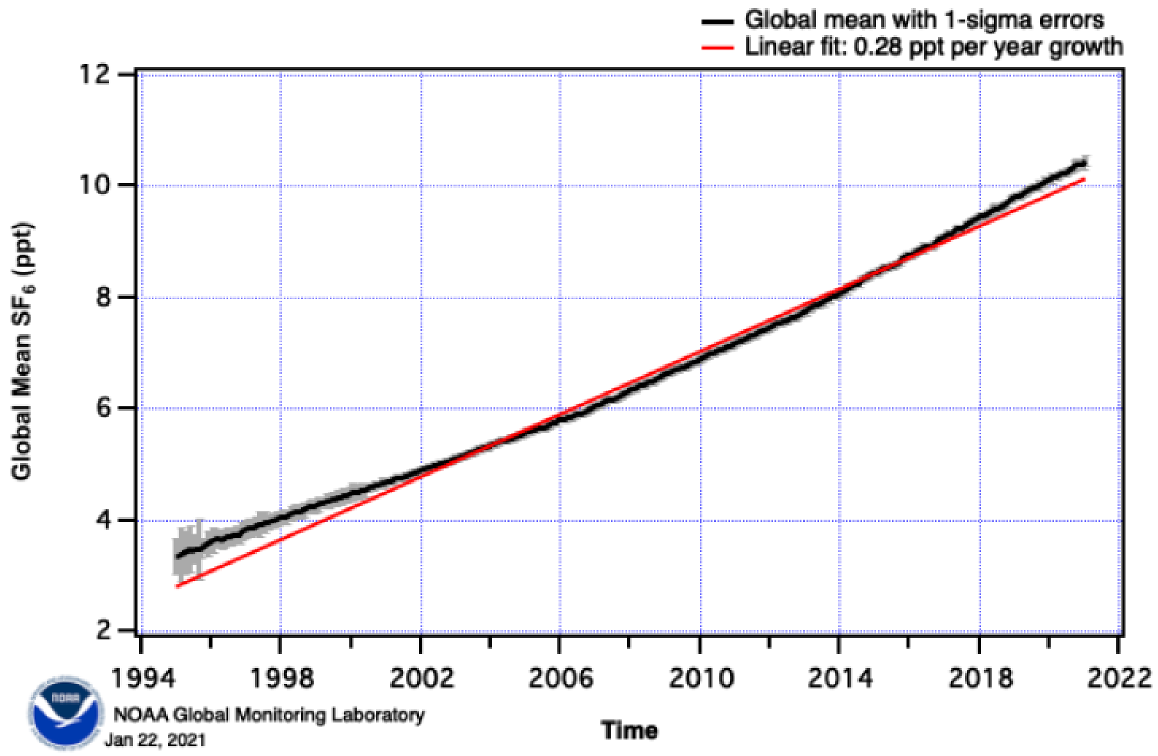
Environmental concerns with SF_6 use
Evolution of SF_6 concentration in the atmosphere



- Intensive measures to avoid SF_6 emission, since long time
- Nevertheless increasing SF_6 concentration in the air
- Review of worlwide regulations is given in the brochure

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Alternatives to SF_6 for electrical insulation

- Non-gaseous insulation: Solid, liquid and vacuum
- Insulation with gases of natural origin
- Synthetic gas, or gas mixtures alternatives

- Technical as well as non-technical requirements on gases are given in the brochure

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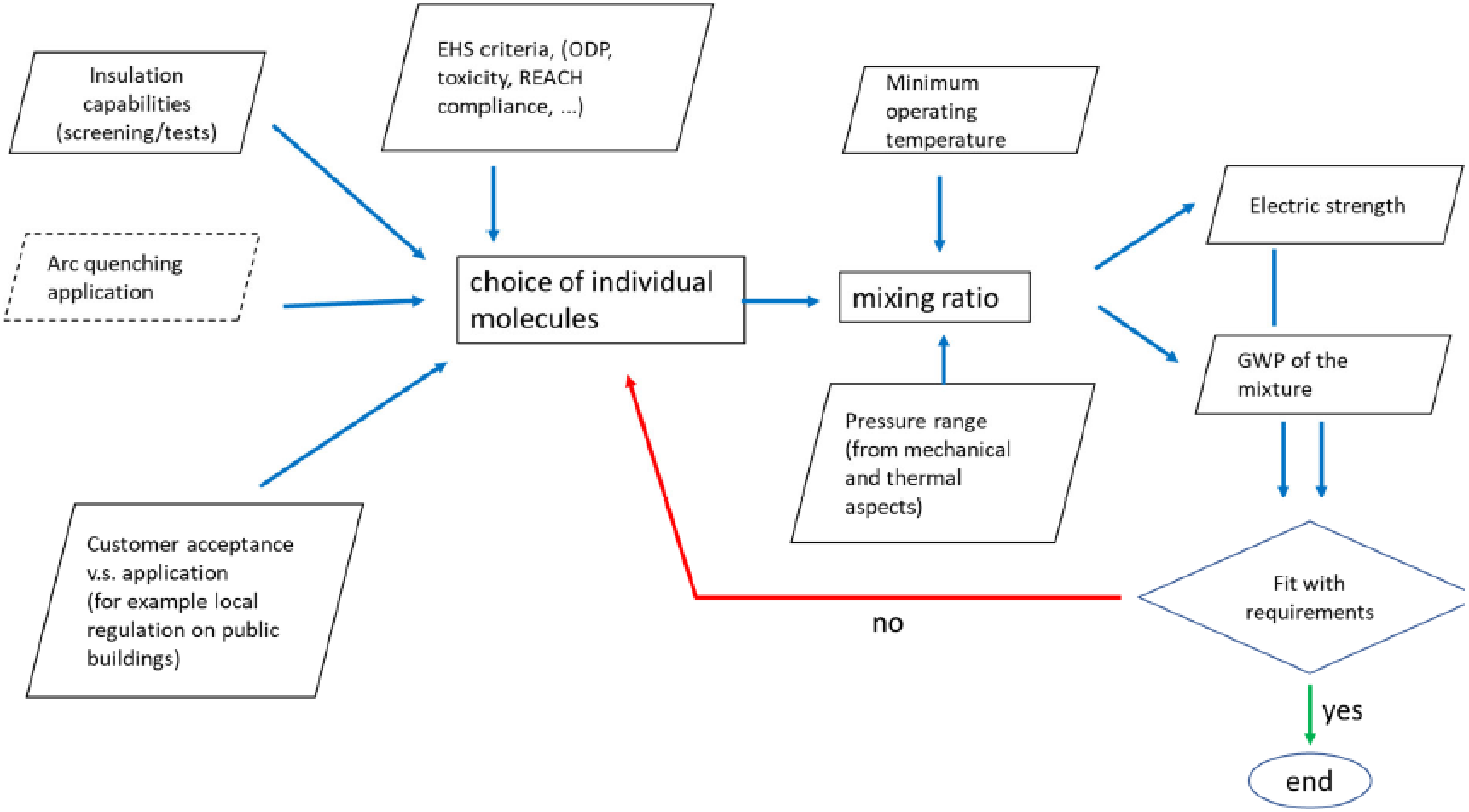
Example of estimation process for the choice of an SF_6 alternative mixture



Description of methods to find new gases

- Screening methods by observing relations of microscopic molecule properties with electric strength and boiling point
  - Summary of studies from 1977 until 2019
  - Overview of descriptors used for the prediction of electric strength (ES) and boiling point (BP)

- Methods for filtering considering environmental and safety aspects

- Dedicated chemical engineering to find latest generation of insulation gases

Methods to characterize gases

- Physical properties
  - Vapour pressure / Boiling points of pure substances
  - Equation of state and pressure-temperature curve for gases and mixtures
    (→ volume / molar concentration ≠ partial pressure filling)
  - Thermodynamic and transport properties
    (enthalpy, specific heat, thermal and electrical conductivity, speed of sound, viscosity)
- Chemical properties and stability
  - Thermal stability
  - Stability under permanent electric stress and partial discharge
  - Stability under X-ray irradiation
- Electron interactions with the gas
- Electric breakdown strength

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Gases selected in this working group

- SF_6
- C4-FN mixtures (in CO_2)
- C5-FK mixtures (in CO_2 and air)
- HFO-1234ze(E)
- CF_3I (mixture)

Pre-Study for natural-origin gases (CIGRE WG D1.51):

"Dry air, N_2, CO_2 and N_2/SF_6 mixtures for gas-insulated systems"
TB 730 (2018)

Summary of know-how on gases and gas mixtures

Property	C4-FN	C5-FK	Trifluoroiodomethane	Hydrofluoolefin 1234 zeE
Chemical formula	$(CF_3)_2CFCN$	$CF_3C(O)CF(CF_3)_2$	CF_3I	$C_3H_2F_4$
Boiling point (°C)	-4.7	26.9	-22.5	-19.4
Molar Mass (g/mol)	195.04	266.04	195.91	114.04
Relative electric strength (% of SF_6)	>200	~200	~119	~ 85
Ozone depletion potential (ODP)	0	0	Very low	0
Global warming potential (GWP)	2100(1)	<1	0.4	<1
Flammability	No	No	No	No according to ASTM E681-01 , to slightly according to ISO 817:2014

(1): depending on the method applied for the calculation of the GWP, this value can vary from 1490 to 3646 [126] [127]

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Summary of know-how on gases and gas mixtures

Property	C4-FN	C5-FK	Trifluoroiodomethane	Hydrofluoolefin 1234 zeE
Thermal stability	Stable up to 700 °C	Stable up to T >500 °C	stable up to 120 °C	Stable up to about 550 °C
Toxicity (LC 50) (ppmV)	>10000 and <15000	>13956 and <20086	Inhalation (rat): LC50 274,000 ppm/15 min Cardiac sensitization (dog): NOAEL[(2)] 2,000ppm; LOAEL[(3)] 4,000ppm	>207000
CAS number	42532-60-5	756-12-7	2314-97-8	29118-24-9
CMR classification [(4)]	Mutagenicity : not mutagen (in vitro). Carcinogenicity – reproductive toxicity : no data are currently available or data are not sufficient for classification	Mutagenicity : not mutagen (in vitro) Carcinogenicity – reproductive toxicity: no data are currently available or data are not sufficient for classification	Mutagenicity: tests showed mutagenic in vitro not in vivo Carcinogenicity : no data are currently available or data are not sufficient for classification. Reproductive toxicity: NOAEC 2%	Mutagenicity : not mutagenic (in vitro and in vivo)
(2): highest dose at which there was not an observed toxic or adverse effect (3): lowest dose at which there was an observed toxic or adverse effect (4): according to ECHA data at date of 11/03/2020				

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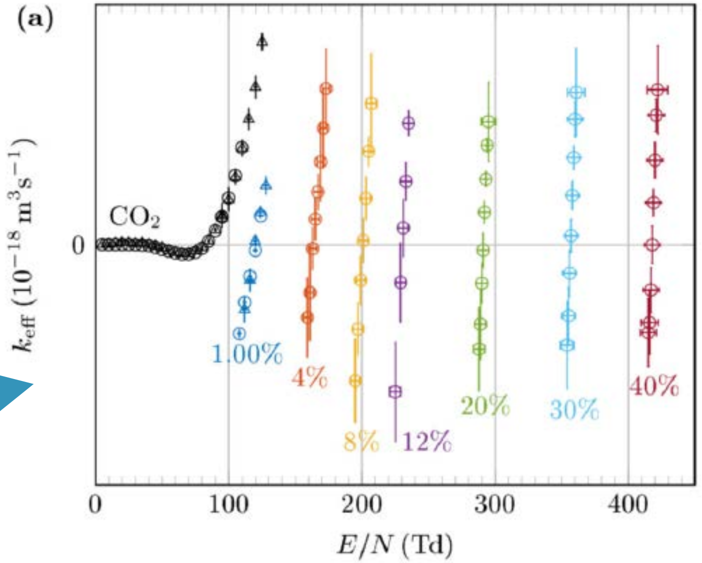
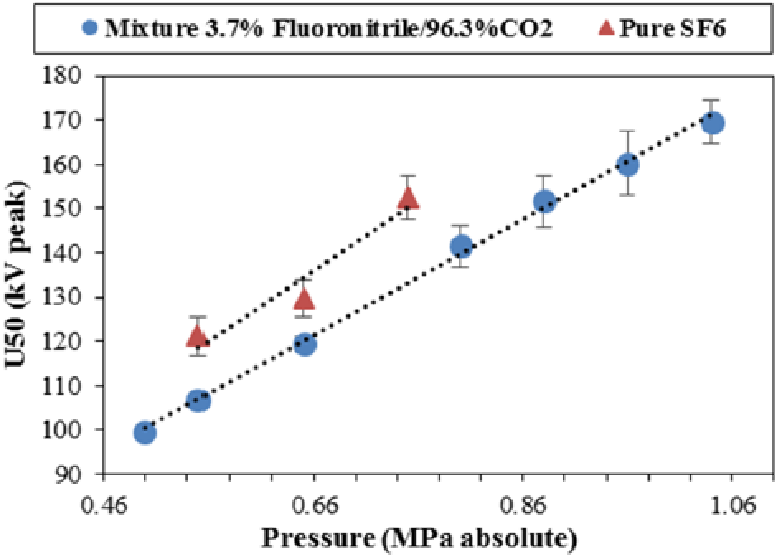
Summary on insulation strength related characteristics

[Status of Summary March 2019]

For all four selected gases and gas mixtures

- Swarm parameters: effective ionization coefficient
- Electric breakdown strength
- Stability of insulation performance
- V-t characteristics (if available)





Detailed values not shown here
→ see Technical Brochure

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Part B

Newly proposed test methods and procedures

Practical Insulation Performance

- Behaviour under non-ideal conditions
  - Non-uniform fields (weakly and strongly)
  - Electrode surface roughness
  - Electrode surface size
  - Partial-Discharge Inception
  - Impulse Voltage Waveshape

➢ determine applicable limiting values for a reliable design of industrial gas-insulated systems

Proposal for practical tests

- electric strength for AC and transient voltages
- electric strength under weakly non-uniform electric fields
- sensitivity to electrode surface conditions and size (i.e. area effect)
- sensitivity to strongly non-uniform electric fields in the form of imperfections such as protrusions and particles
- relation between AC and LI breakdown strengths
- test conversion factors according to IEC 60071-1

Definition of a representative test parameter set

	MV	HV
Typical gap distance	25 - 60 mm	30 – 100 mm *
Chosen reference gap distance	**10 mm (±1%)**	**15 mm (±1%)**

Weakly non-uniform arrangement	MV	HV
Typical degree of homogeneity	η = 0.15 – 0.5	η = 0.45 – 0.8

Strongly non-uniform	MV and HV
Sharp edges	η = 0.05-0.15
Protrusions	η = 0.01-0.05

	MV	HV
Typical surface quality	R_t =15 – 50 µm	R_t = 15 – 50 µm
Chosen reference surface quality	**R_t = 50 µm (±2 µm)**	**R_t = 20 µm (±2 µm)**

	MV	HV
Typical pressure (absolute)	0.12 - 0.16 MPa	0.5 - 0.8 MPa
Chosen reference (absolute)	**0.13 MPa**	**0.6 MPa**

Definition of a representative test parameter set

	MV	HV
C4-FN	was not proposed for MV application	5% C4-FN / 5% O_2 / 90% CO_2
C5-FK	13.5% C5-FK / 17.3 % O_2 / 69.2% N_2	5.5 C5-FK / 11.2 % O_2 / 83.3% CO_2
CF_3I	30% CF_3I / 70% CO_2	30% CF_3I / 70% CO_2
HFO	100% HFO1234ze(E)	was not proposed for HV application

	Minimum Temperature	Reference
MV GIS indoor	-5°C	IEC 62271-200
MV GIS outdoor	-25°C	62271-200
HV GIS outdoor	-25 °C / -40°C	IEC 62271-203
HV GIS only indoor	-5 °C / -25°C	IEC 62271-203
HV AIS	-30 °C	IEC 62271-100
HV GIL (tunnel installation)	-10 °C	IEC 62271-204
HV Special application in cold countries	-50 °C	IEC 62271-1

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Recommended tests

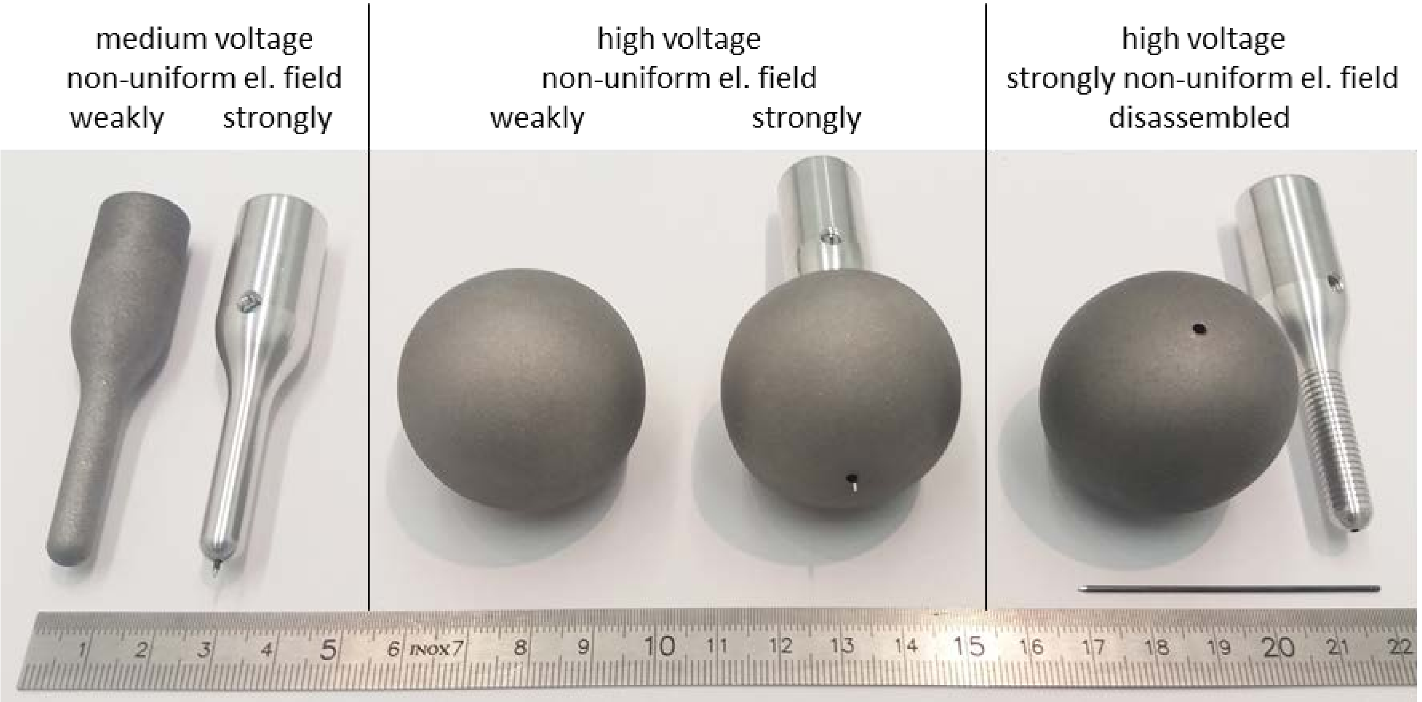
(these were also performed within this working group)

Pre-study with AC: Mixture and pressure screening in homogenous arrangement

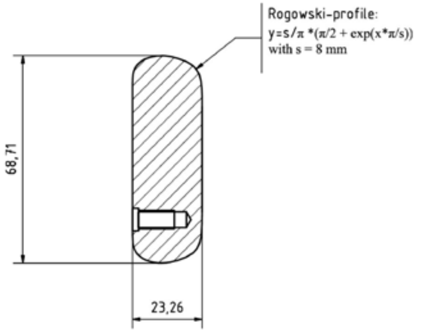
Test 1: AC withstand voltage test in weakly non-uniform arrangement

Test 2: Lightning impulse breakdown test in weakly non-uniform arrangement

Test 3: Lightning impulse breakdown test in strongly non-uniform arrangement



Always a Rogowski-profile was used as low-voltage electrode



Recommended tests

(these are recommended but were not performed within this working group)

Test 4: **AC** breakdown test in **strongly non-uniform** arrangement

Test 5: **AC** breakdown in weakly non-uniform arrangement with **varying surface size**

Test 6: **Switching impulse** breakdown test in **strongly non-uniform** arrangement

Test 7: **AC** breakdown test in uniform arrangement with **varying surface roughness**

Test 8: **LI** breakdown test in uniform arrangement with **varying surface roughness**

Test 9: **PD** activity in **strongly non-uniform arrangement**

Test 10: **PD** measurement in quasi-uniform arrangement with **particle on insulator**

Test 11: **AC** breakdown voltage after **ageing of gas**

Test 12: Withstand voltage under **VFT conditions**

Test 13: **PD** measurement with **hopping particle** attached to HV electrode

Test 14: **AC** breakdown in uniform arrangement with insulator at **varying humidity**

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Definition of protocol and measurement guidelines

- Very detailed step-by-step documentation of
  - ✓ **experimental setup**
  - ✓ **preparation procedure**
  - ✓ **experiment execution**
  - ✓ **documentation procedure**

- Template for measurement protocol.

(all available for future use at https://doi.org/10.3929/ethz-b-000482801)

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Part C

Electrical Insulation Strength of novel gas mixtures

Overview

«Part C: Electrical Insulation Strength of novel gas mixtures»

- Data Evaluation Methods and Example Results
- Test Data Analysis
  - SF_6
  - C4-FN mixtures
  - C5-FK mixtures (in CO_2 and air)
  - HFO-1234ze(E)
  - CF_3I (mixture)
- Summary & Conclusion (Part C)

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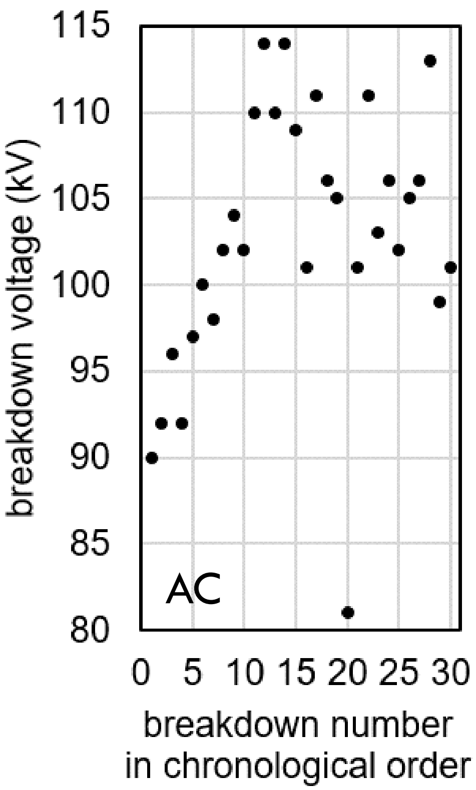
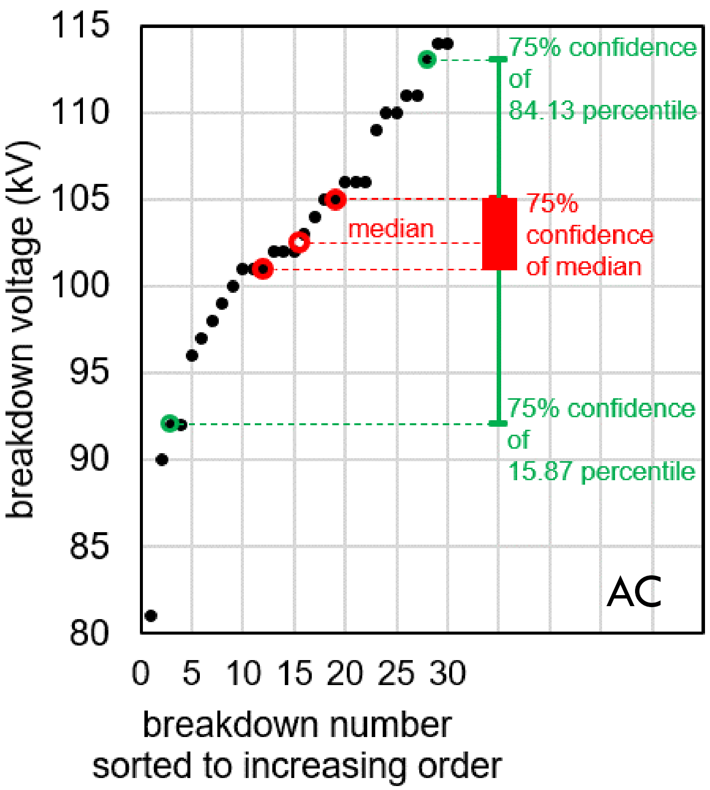
Data Evaluation Methods

AC voltage rise breakdown test





- Sort by breakdown voltage
- Median (incl. confidence interval)
- 16 and 84 percentiles (with 75% confidence)

[H. Schmid, IEEE Solid-State Circuits Magazine 6(2), 52 (2014)]

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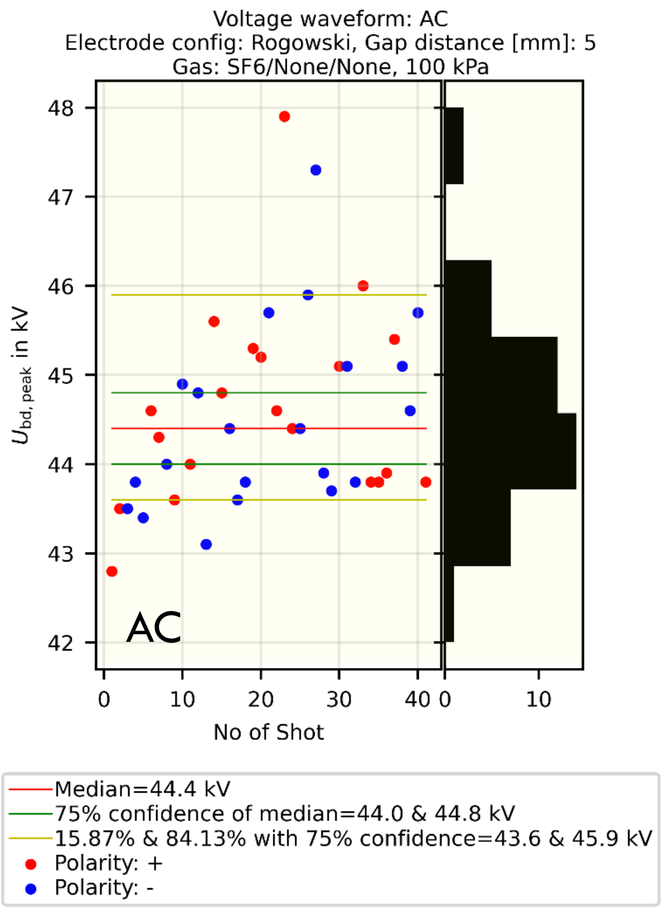
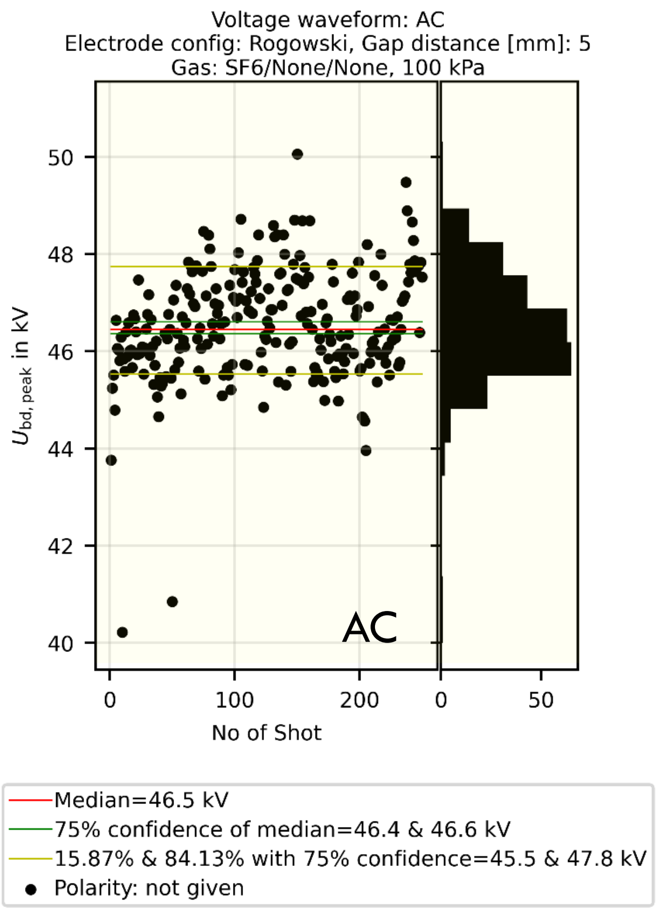
Data Evaluation Method Examples

AC voltage rise breakdown test





- Good examples
- «conditioning» effect for first few shots may be present
- ≥ 30 shots seems reasonable

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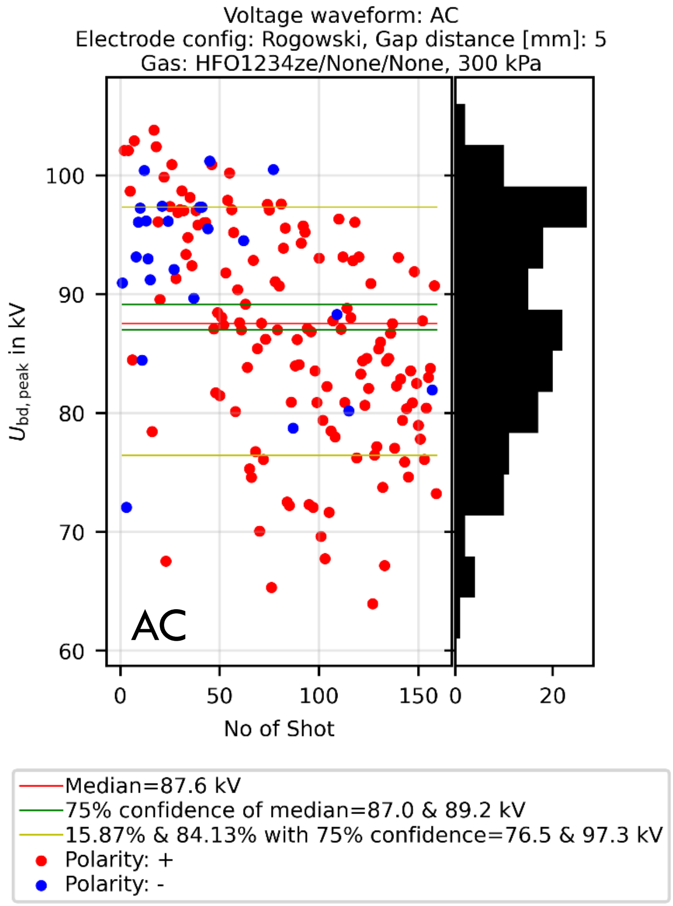
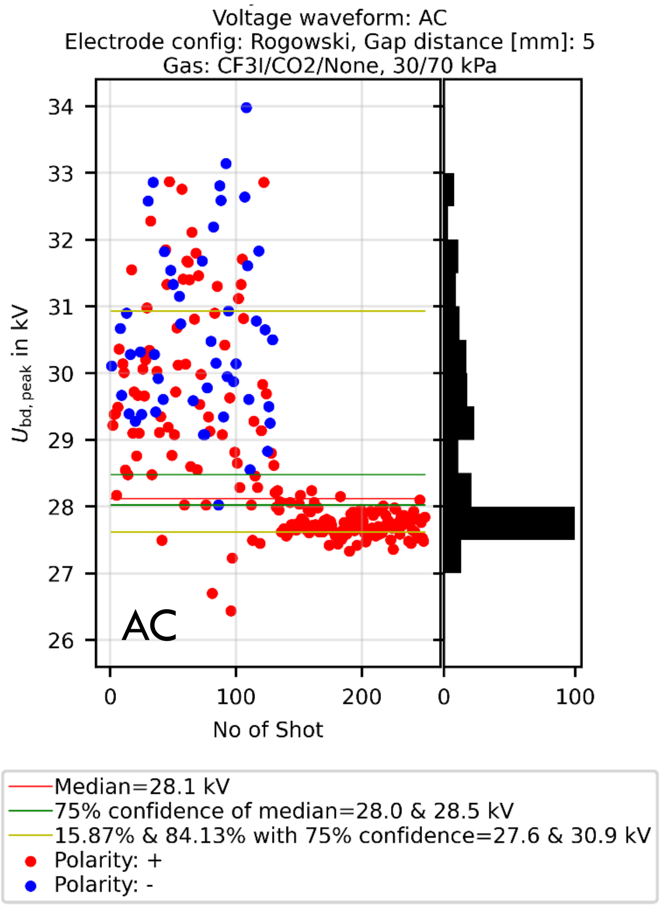
Data Evaluation Method Examples

AC voltage rise breakdown test





- «Bad» examples
- Decreasing or increasing trends
- Polarity despite uniform field not randomly distributed

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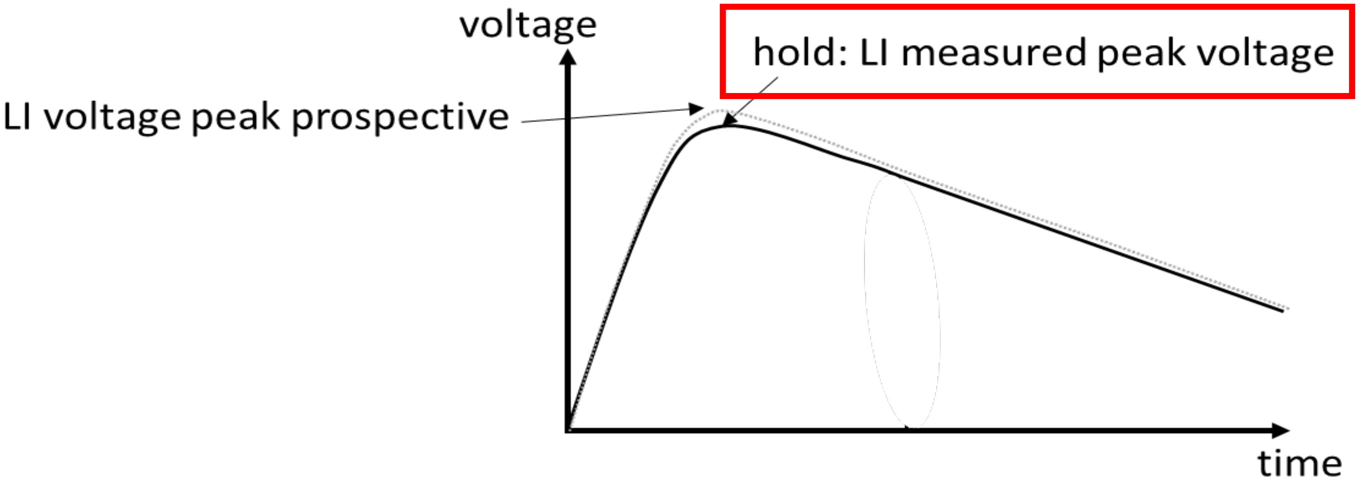
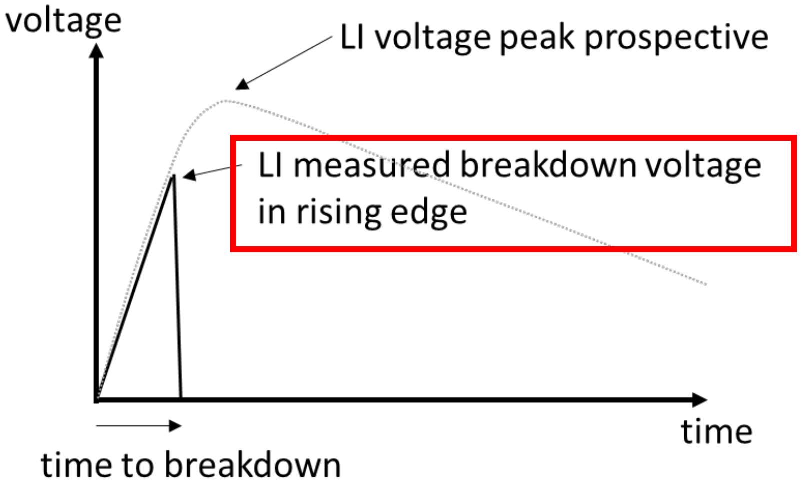
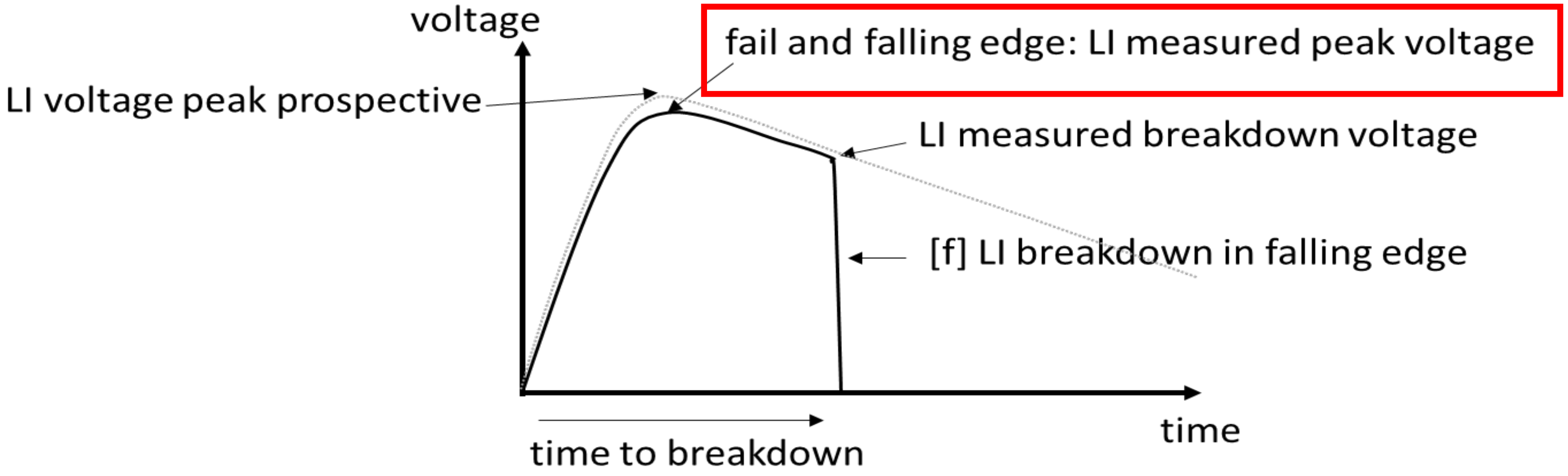
Data Evaluation Methods

LI voltage data evaluation

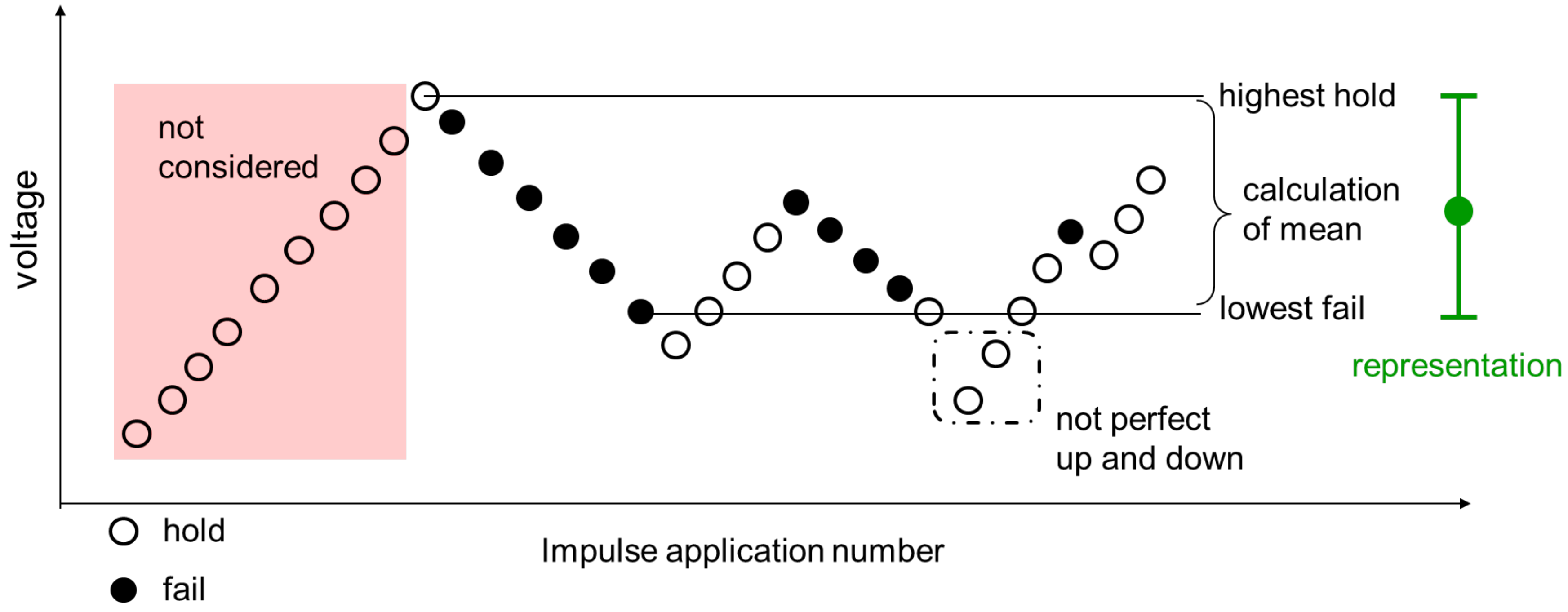






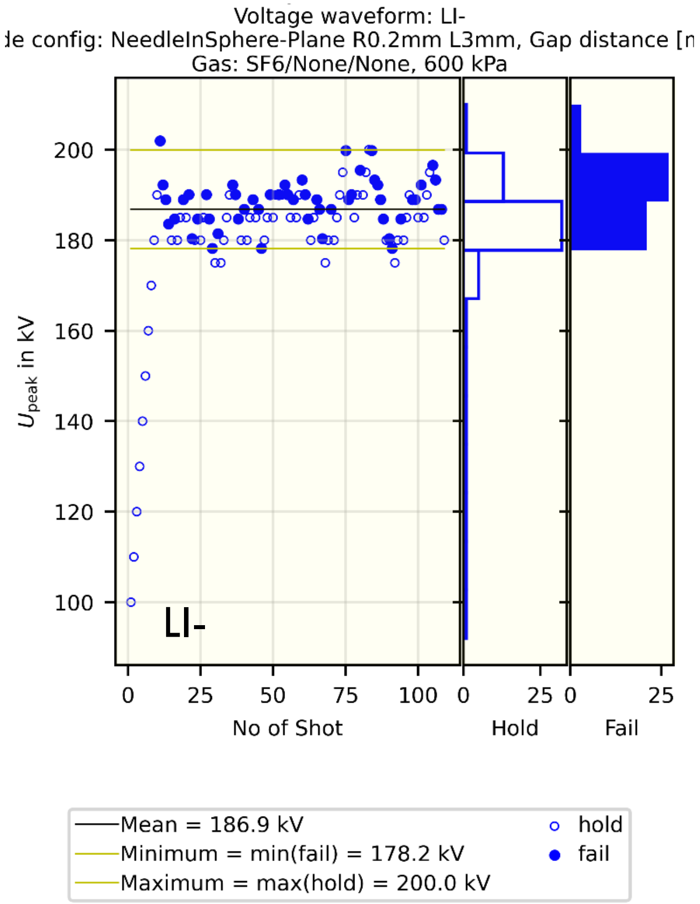
Data Evaluation Methods

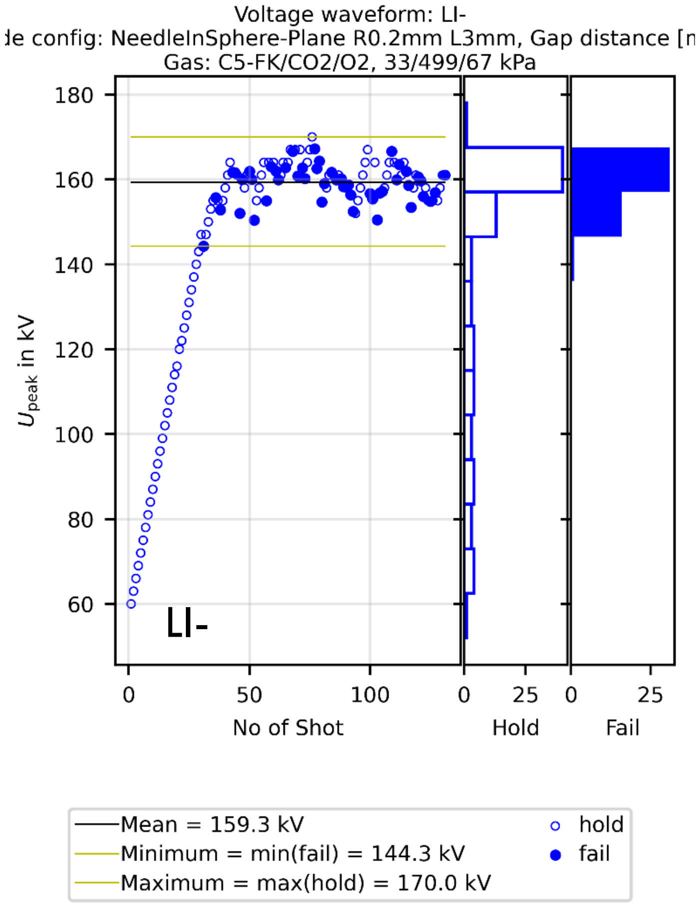
LI voltage data evaluation



Data Evaluation Examples

LI voltage data evaluation





- Good examples

(even though starting value is very low)

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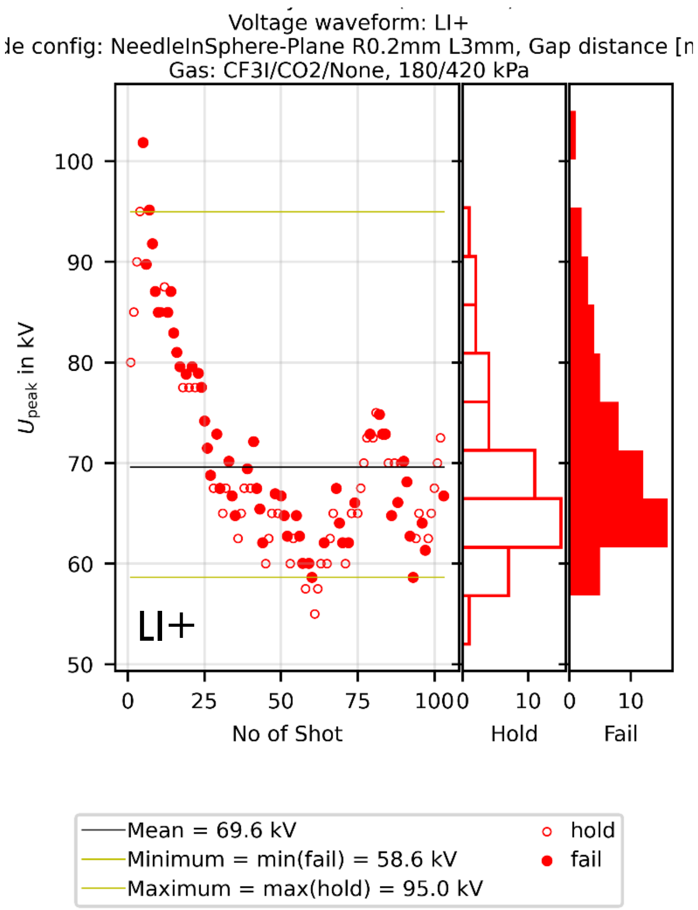
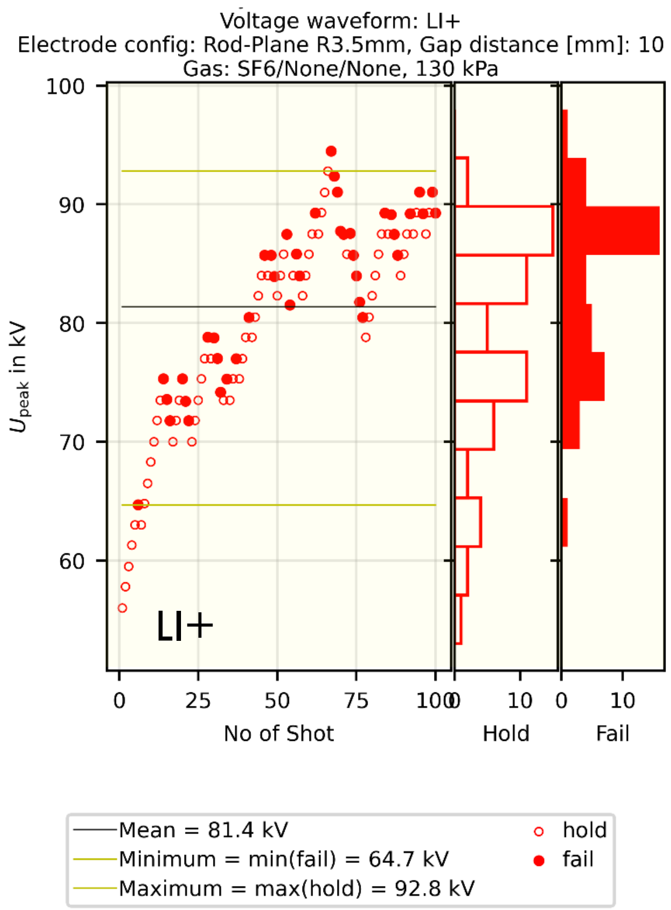
Data Evaluation Examples

LI voltage data evaluation





- «Bad» examples
- Typically increasing or decreasing trend

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Fundamentals of Electric Breakdown in Strongly Attaching Gases

(as known from SF_6, to be shown if also present in new gas mixtures)

- Initial electron
  (radiation ionization, detachment, cathode surface emission)
- Primary avalanche
- Secondary avalanches and Generation Mechanism
- Streamer Initiation
- Streamer Propagation
- Streamer-to-leader transition
- Leader Breakdown

  - ➢ The chosen test geometries and arrangements should allow to study all these different mechanism.

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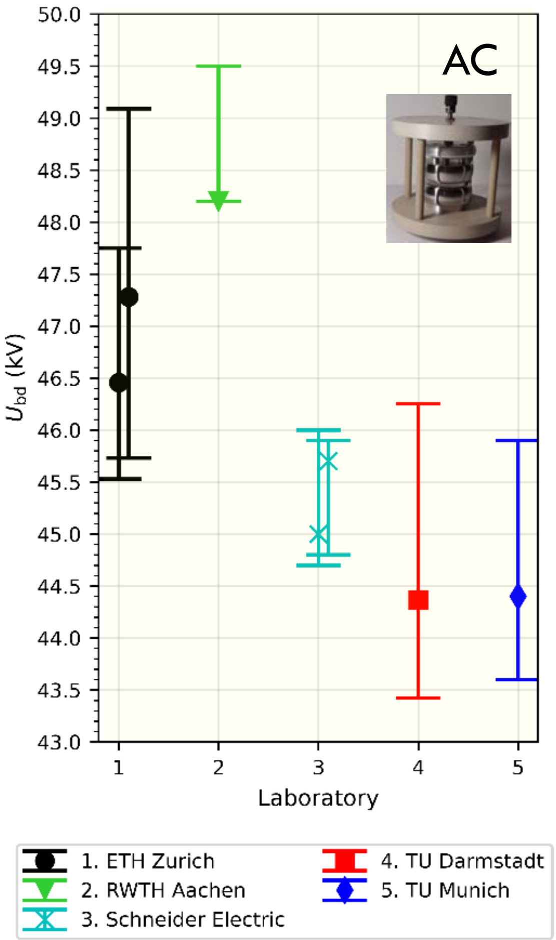
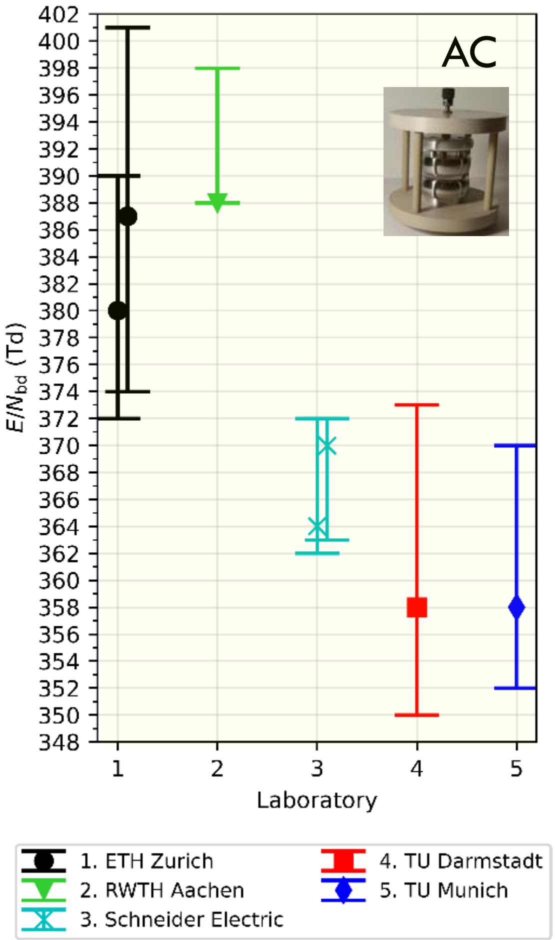
Results for SF_6





- SF_6 is well studied and used as reference gas
- Identify all basic breakdown processes
- Benchmark for inter-lab comparison

- Reasonable agreement in between labs
- ~ 15 % uncertainty
- Reasonable agreement to literature

AC breakdown in uniform electric field (1 bar, 5 mm)
(all data points, no need to reassess)

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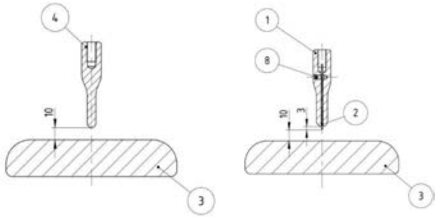
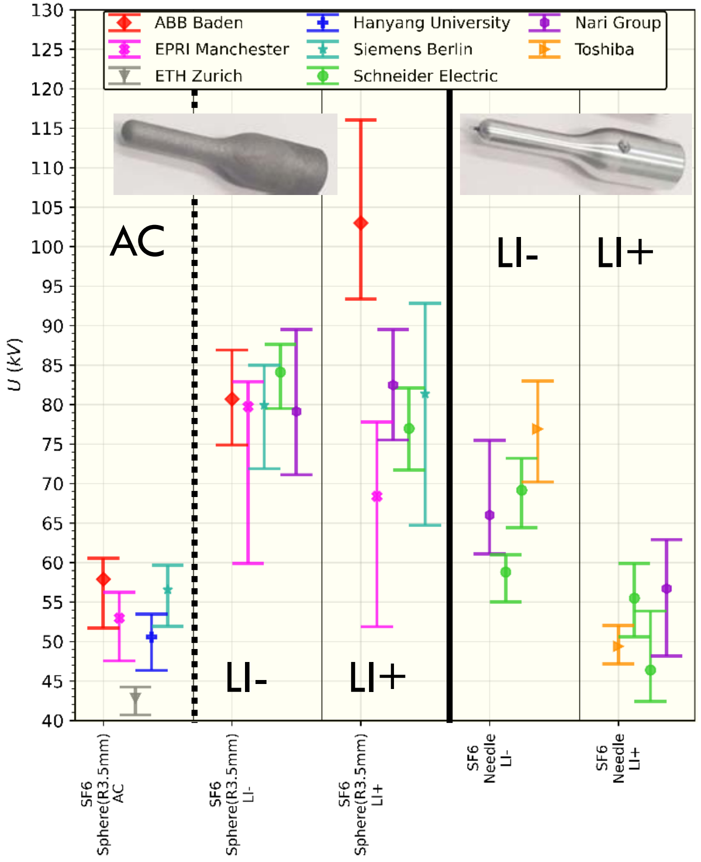
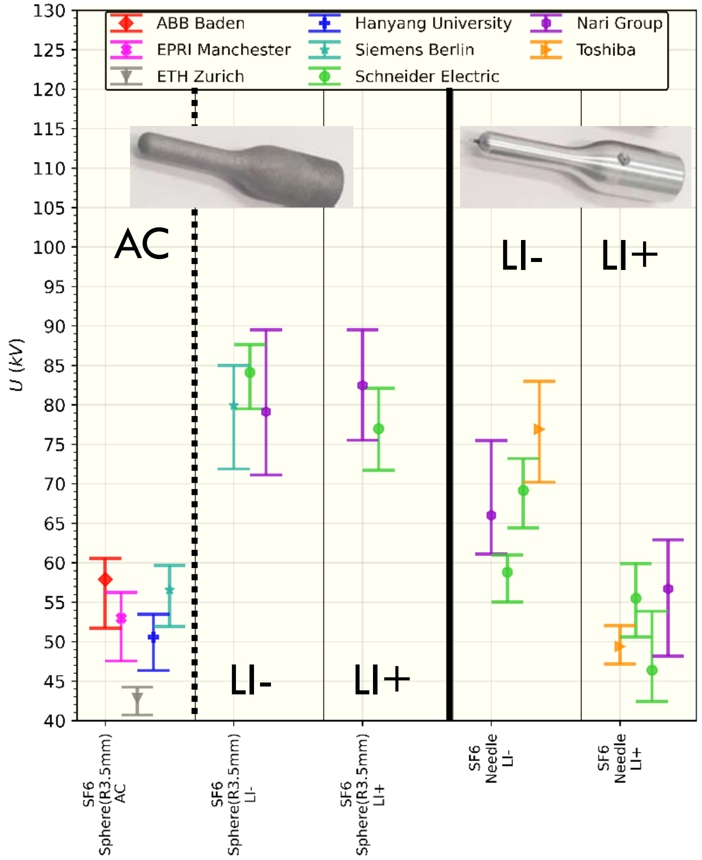
Results for SF_6







- Even for SF_6, some test series had to be excluded from the evaluation.
- Inter-laboratory comparison shows significantly increased scatter.

Results for “practical insulation performance MV”
(left: all data, right: reassessed)

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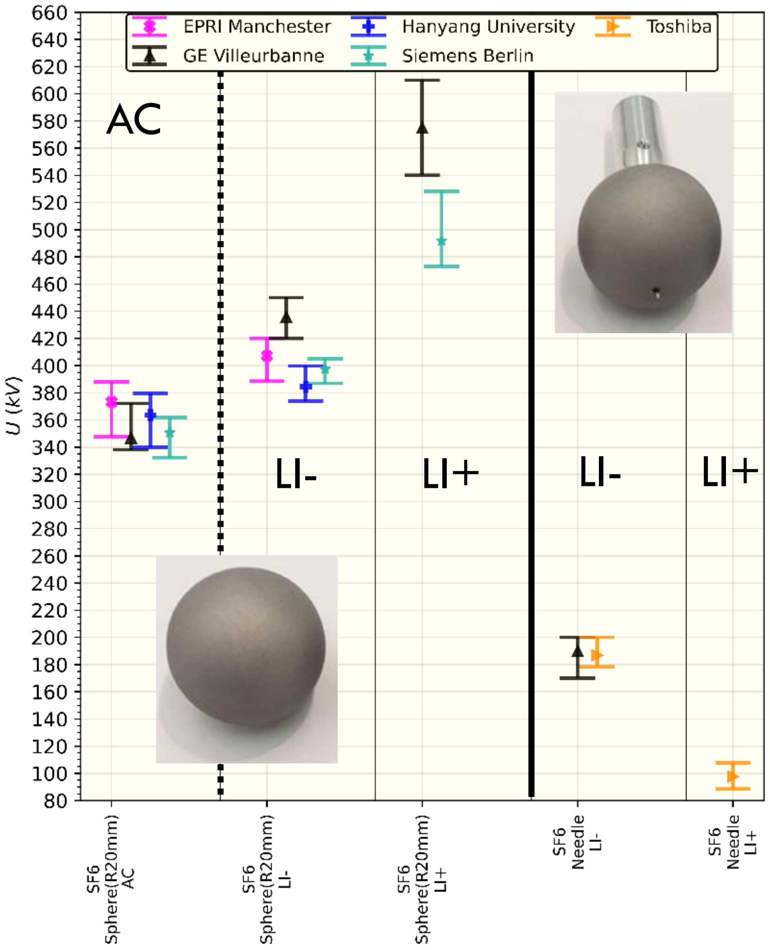
Results for SF6



- Only few labs performed HV test with SF_6. (dedicated gas handling equipment needed)
- Inter-laboratory comparison best for AC voltage
- Largest scatter for LI positive.

Results for "practical insulation performance HV"
(only reassessed)

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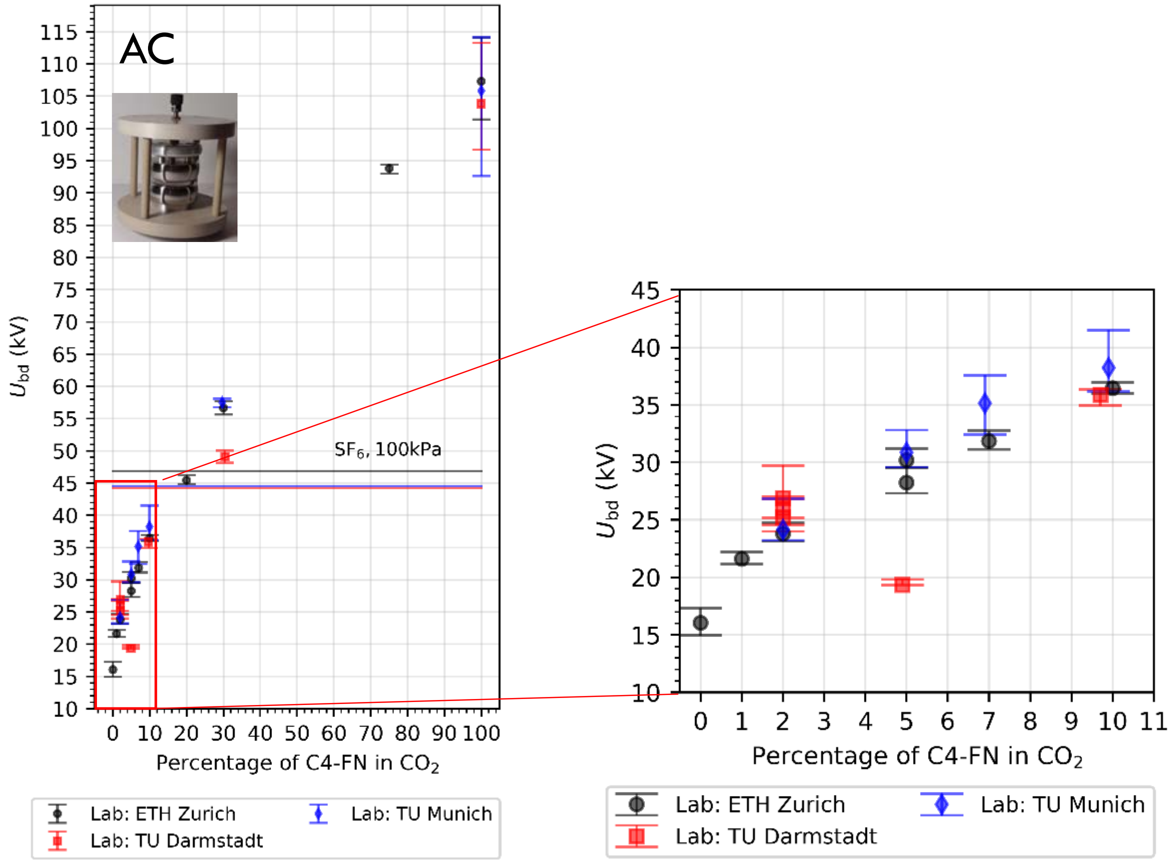
Summary: SF_6 measurements

- Chosen geometries suited to test for all breakdown phenomena
- In general good inter-laboratory agreement.
- Even in SF_6 some measurement series shown trends and thus, measurements have to be carefully questioned always.
- Application of purging voltage between shots has significant influence (maybe even effect of different background radiation can be seen)

Results for C4-FN (mixtures)



- Strong synergy, especially < 10 %
- With 20% similar to SF_6

Mixing ratio scan of C4-FN in CO_2 at 100 kPa in uniform field.
(both: reassessed data)

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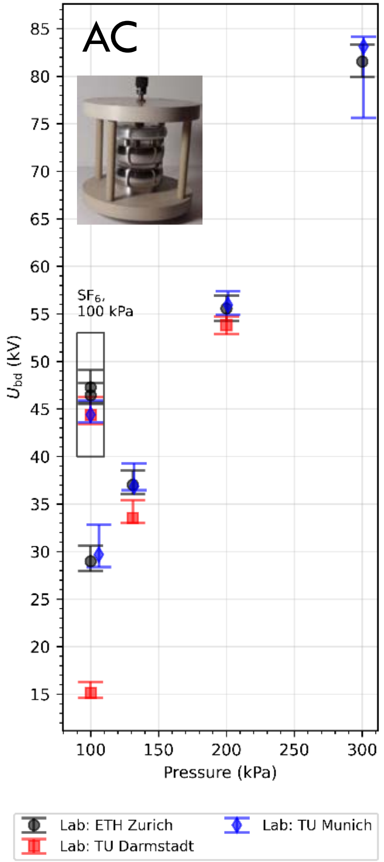
Results for C4-FN (mixtures)



- Linear increase with pressure
- At 100 kPa approx. 65% of SF_6
- With ~170 kPa similar to SF_6 at 100 kPa

Pressure scan of 5% C4-FN in CO_2 in uniform field.
(reassessed data)

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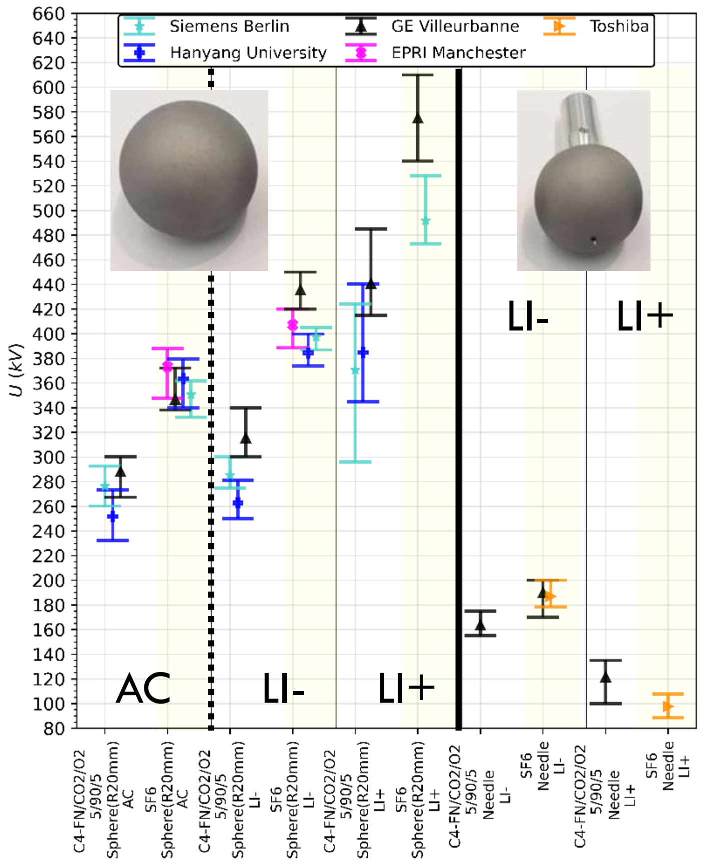
Results for C4-FN (mixtures)



Practical Insulation Performance HV of C4-FN
(reassessed data)

- In general good inter-laboratory comparability
- For LI similar behaviour as SF6
  - Weakly non-uniform: $U_{LI+} > U_{LI-}$
  - Strongly non-uniform: $U_{LI+} < U_{LI-}$

Summary: C4-FN measurements

- breakdown voltages in the C4-FN mixture showed similar trends to those in SF_6
- no unexpected effects were observed
- gas mixture can be considered self-restoring

  - ➢ Existing test and design rules, known from SF_6, can be similarly applied to C4-FN mixtures when scaled with the ratio of electric strength.

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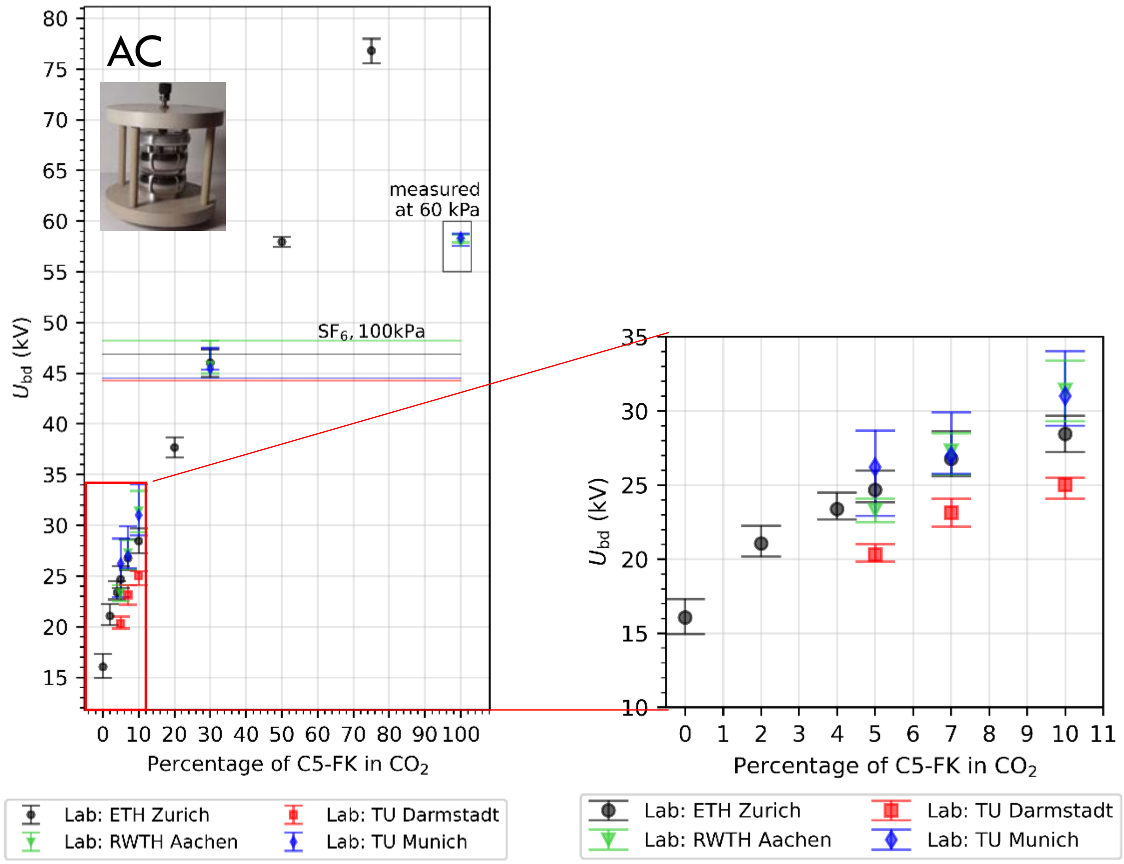
Results for C5-FK (mixtures in CO_2)



- One lab consistently lower (no plausible reason found)
- Due to boiling point 100% not measureable
- Strong synergy, especially < 10 %
- With 30% similar to SF_6

Mixing ratio scan of C5-FK in CO_2 at 100 kPa in uniform field.
(both: reassessed data)

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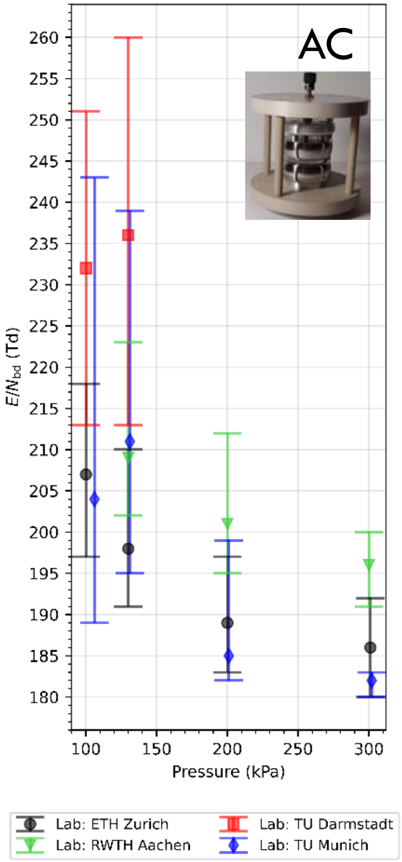
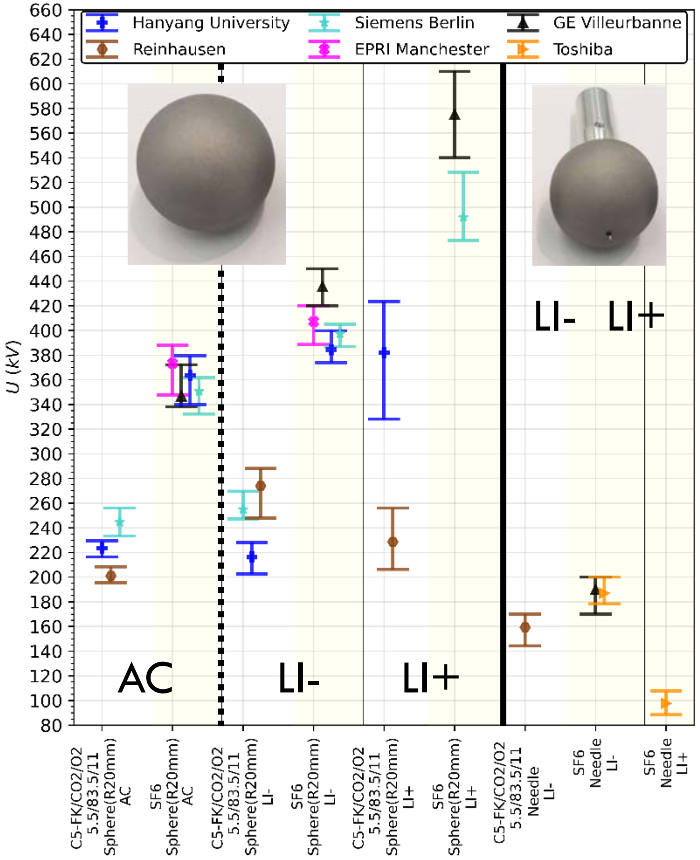
Results for C5-FK (mixtures in CO2)



- Breakdown field almost constant 100-300 kPa
- At 100 kPa approx. 55% of SF_6

Pressure scan of 5.5% C5-FK in CO_2 in uniform field.
(reassessed data)

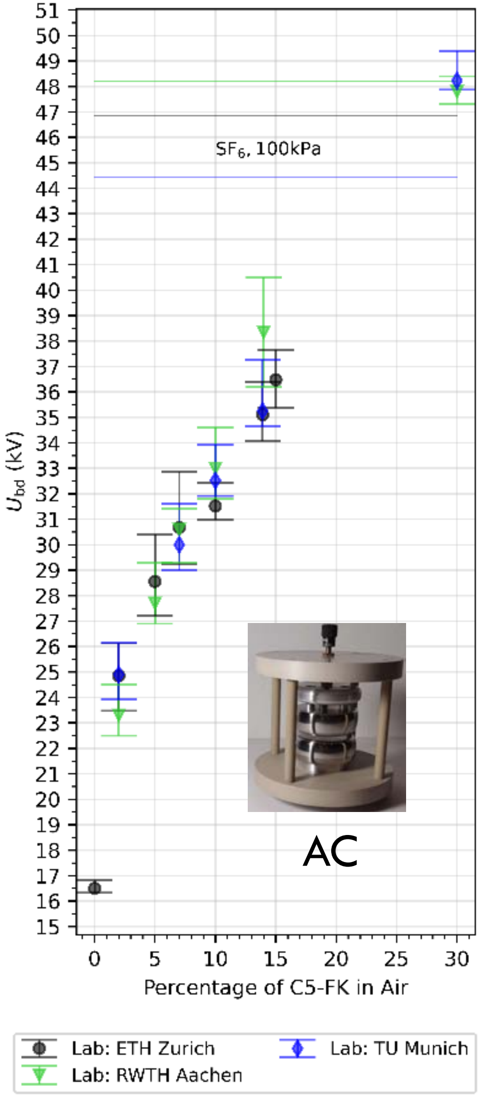
Results for C5-FK (mixtures in CO2)



- In general good inter-laboratory comparability (one exception)
- For LI similar behaviour as SF6
  - Weakly non-uniform: $U_{LI+} > U_{LI-}$ (one exception)
  - Strongly non-uniform: $U_{LI+} < U_{LI-}$

Practical Insulation Performance HV of C5-FK / CO_2 mixture
(reassessed data)

Results for C5-FK (mixtures in air)



- Electric strength in air slightly higher than in CO_2.
- Strong synergy, especially < 10 %
- With ~30% similar to SF_6

Mixing ratio scan of C5-FK in air at 100 kPa in uniform field.
(reassessed data)

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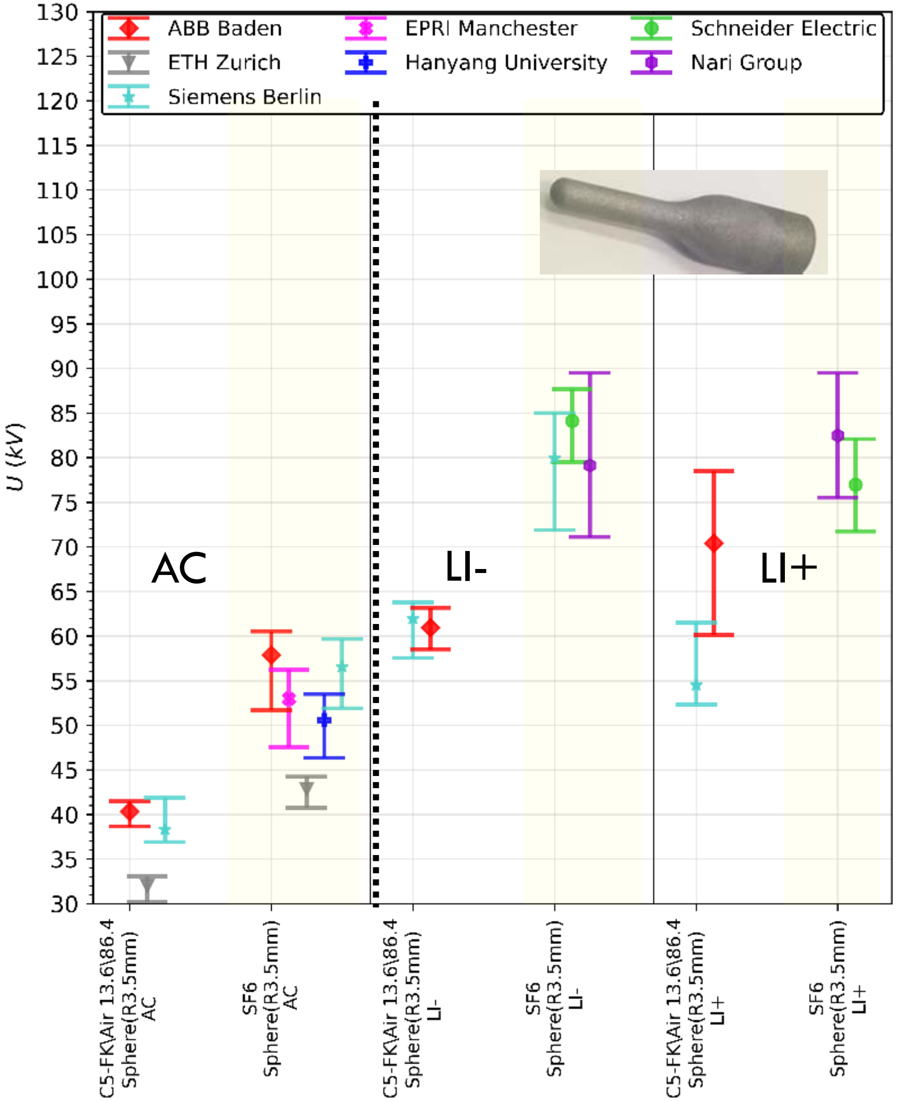
Results for C5-FK (mixtures in air)



- In general good inter-laboratory comparability
- Chosen gas mixture has ~70% withstand strength as SF_6
- Effect of purging in between shots clearly visible for LI+

Practical Insulation Performance MV of C5-FK / air mixture
(reassessed data)

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Summary: C5-FK measurements

- Breakdown voltages in the C5-FK mixture showed similar trends to those in SF_6
- No unexpected effects were observed
- Gas mixture can be considered as self-restoring

➢ Existing test and design rules, known from SF_6, can be similarly applied to C5-FK mixtures when scaled with the ratio of electric strength.

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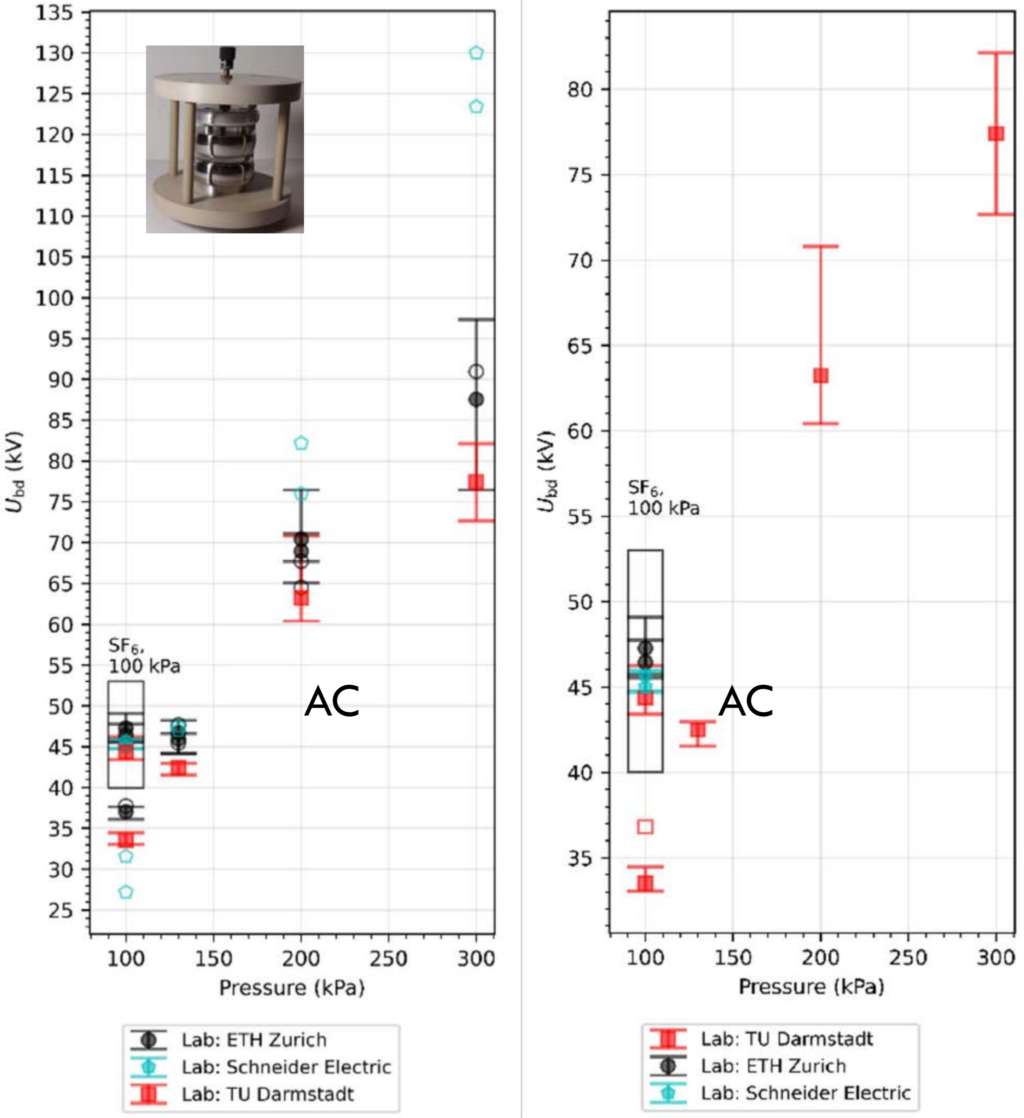
Results for HFO 1234ze(E)



- Empty markers show «first» breakdown
- Full markers are evaluation of full series
- For some labs: large difference between first and consecutive breakdowns.
- Linear increase with pressure
- At 100 kPa ~70-85% of SF_6

Pressure scan of HFO in uniform field.
(left: all data, right: reassessed)

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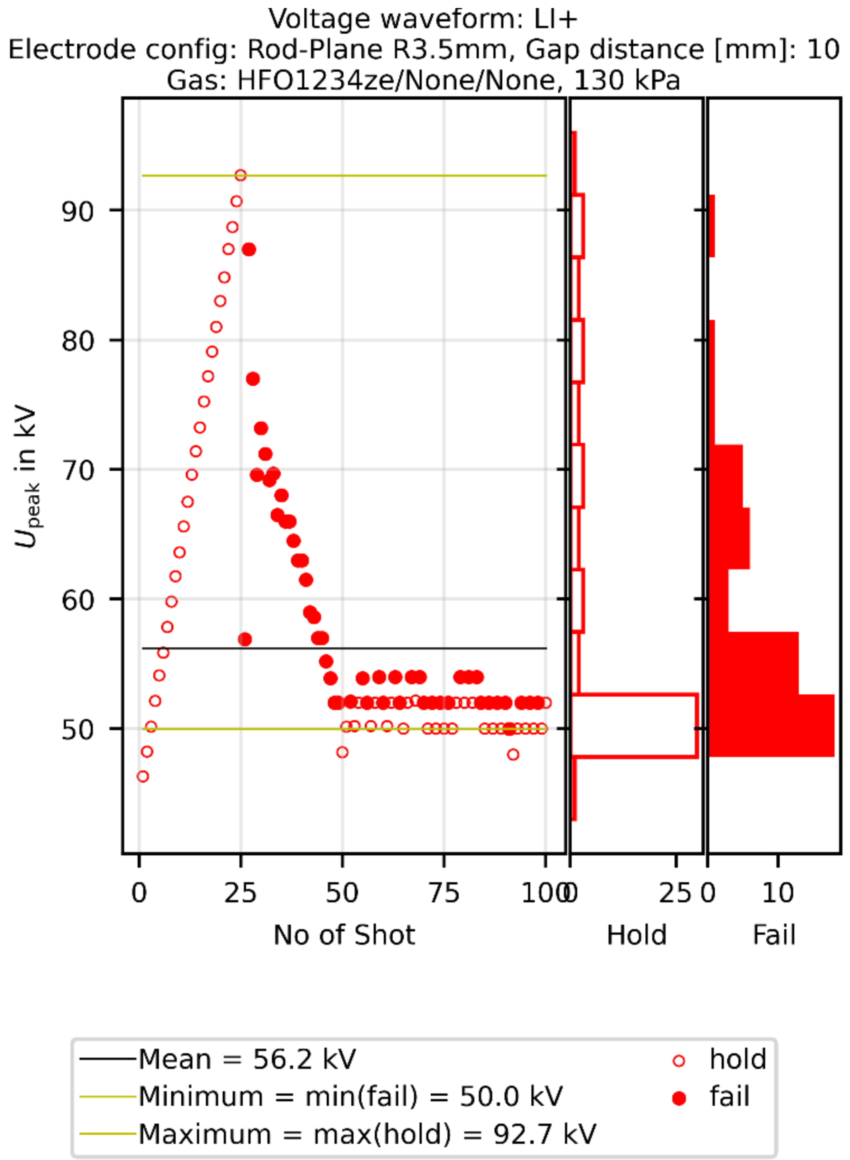
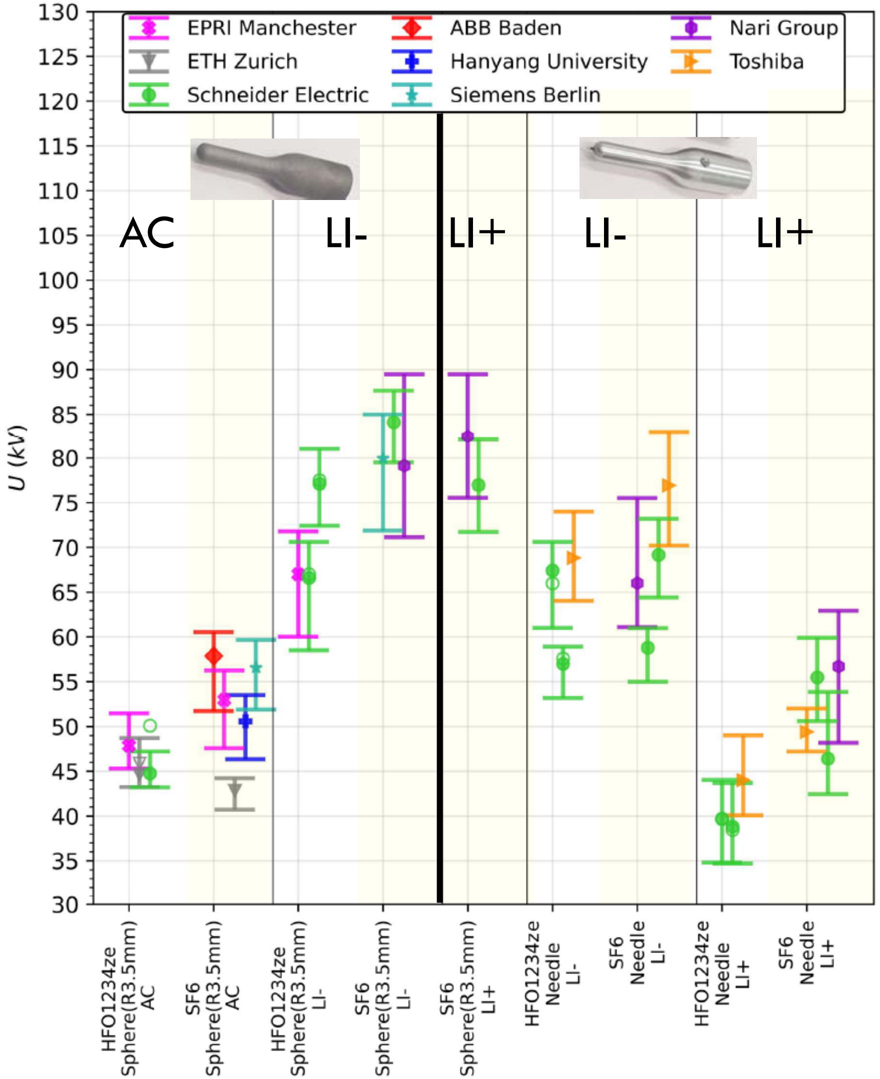
Results for HFO 1234ze(E)



- Strong degradation effects observable
  - ➢ Non-self-restoring gas

Results for HFO 1234ze(E)



- For AC good inter-laboratory comparability
- Large scatter for LI weakly non-uniform measurements
- Strongly non-uniform: $U_{LI+} < U_{LI-}$
- Soot deposit in test vessels, strongly influencing LI+ tests

Practical Insulation Performance MV of HFO1234ze(E)
(reassessed data)

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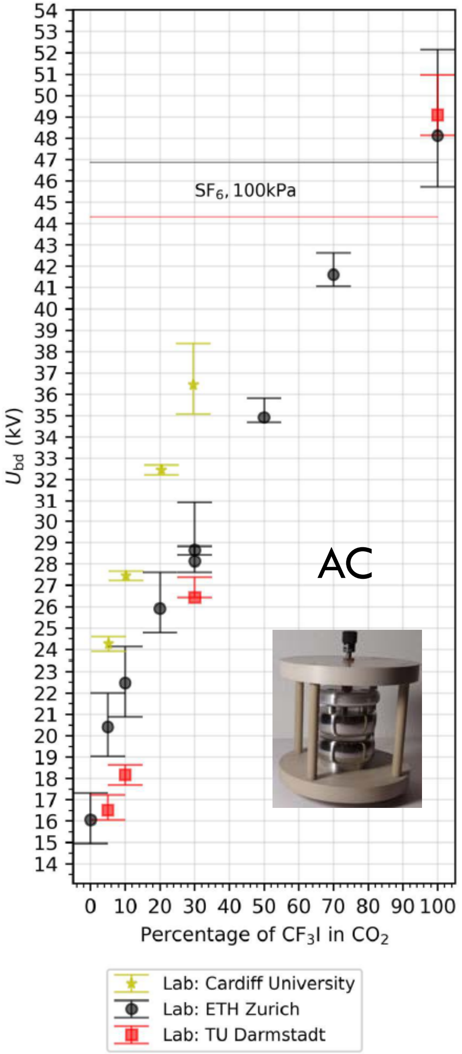
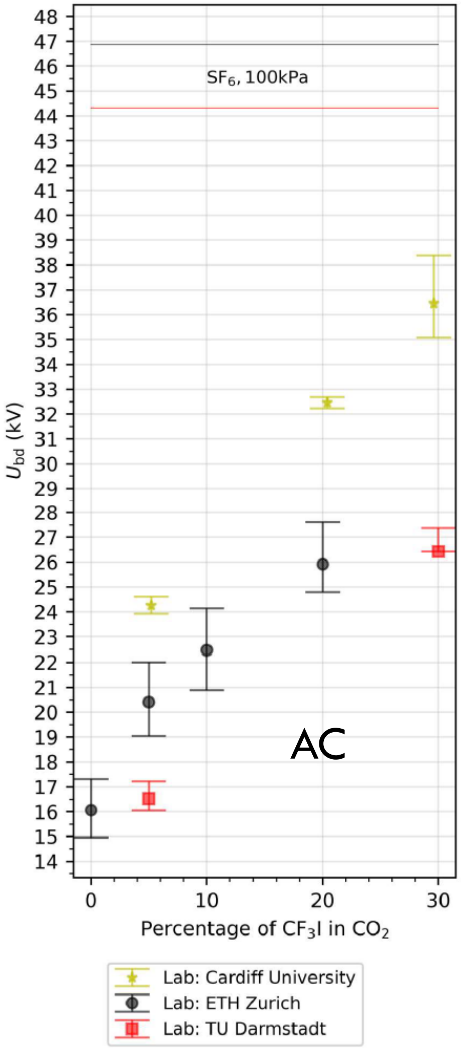
Summary: HFO 1234ze(E) measurements

- Gas decomposition occurs in all tests and is visible as “soot” on electrodes
  (test circuits with strong energy input limitation are essential)
- Some tests strongly influenced by decomposition products, though not all gas mixture should be considered as non-self-restoring

  - ➢ Progressive test stress procedures more suited to test this gas.
  - ➢ Gas suited for insulation purposes only
  - ➢ Additional design margin required to prevent any flashover.

Results for CF_3I





- Gas shows strong decomposition and formation of sticky deposition layer on electrodes
  (stronger at higher mixing ratios and pressure)
- One lab systematically above two others
- Many test series had to be excluded.

➢ No unambiguous conclusion can be derived.

Mixing ratio scan of CF3I in CO_2 at 100 kPa in uniform field.
(left: all data, right: reassessed)

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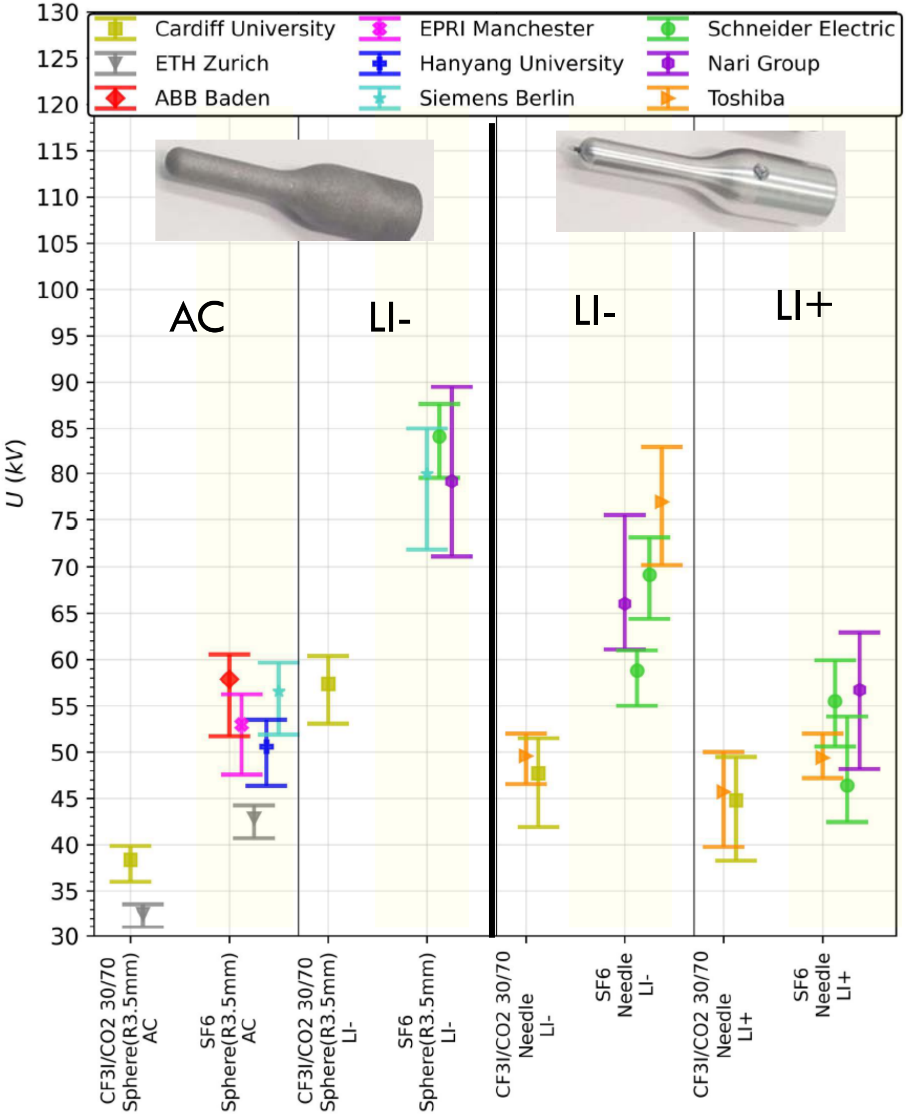
Results for CF_3I



- Again, many test series had to be excluded.
- No valid test series for weakly non-uniform LI+
- Best comparison for strongly non-uniform LI test
  - $U_{LI+} < U_{LI-}$

➢ No unambiguous conclusion can be derived.

Practical Insulation Performance MV of CF_3I in CO_2
(reassessed data)

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Summary: CF_3I measurements

- Strong gas decomposition with sticky layers on electrodes observed.
- Gas mixture should be considered as non-self-restoring

- If considered for application: material compatibility tests should precede experimental campaigns.

  - Test series proposed by WG D1.67 unsuitable to investigate this gas mixture.

Part D

Gas Mixture Analysis

Round robin gas analysis campaign

- New gas mixtures contain small amounts (around 5%) of compounds that dominate the electric strength.

  → accurate mixing and determination of mixing ratio important

- Round robin tests performed on 2 gas mixtures

  - ✓ **Samples prepared centrally**
  - ✓ **Shipped in sample bottles**
  - ✓ **Analysed in (up to) 7 laboratories**
    (gas chromatography –(mass spectroscopy), FTIR

C4-FN / O_2 / CO_2 mixture (5% / 5% / 90%)

- Prepared with commercial mixing unit
- Composition measured with mobile analyser after mixing (5.07 %mol / 5.17 %mol / rest)
- Liquefied and transferred to 50l shipping bottle
- On distribution site: evaporated into 1000 l vessel and mixed (measured to be 5.3 %mol / 5.42 %mol / rest)
- Filled smaller sample bottles and transfer to labs

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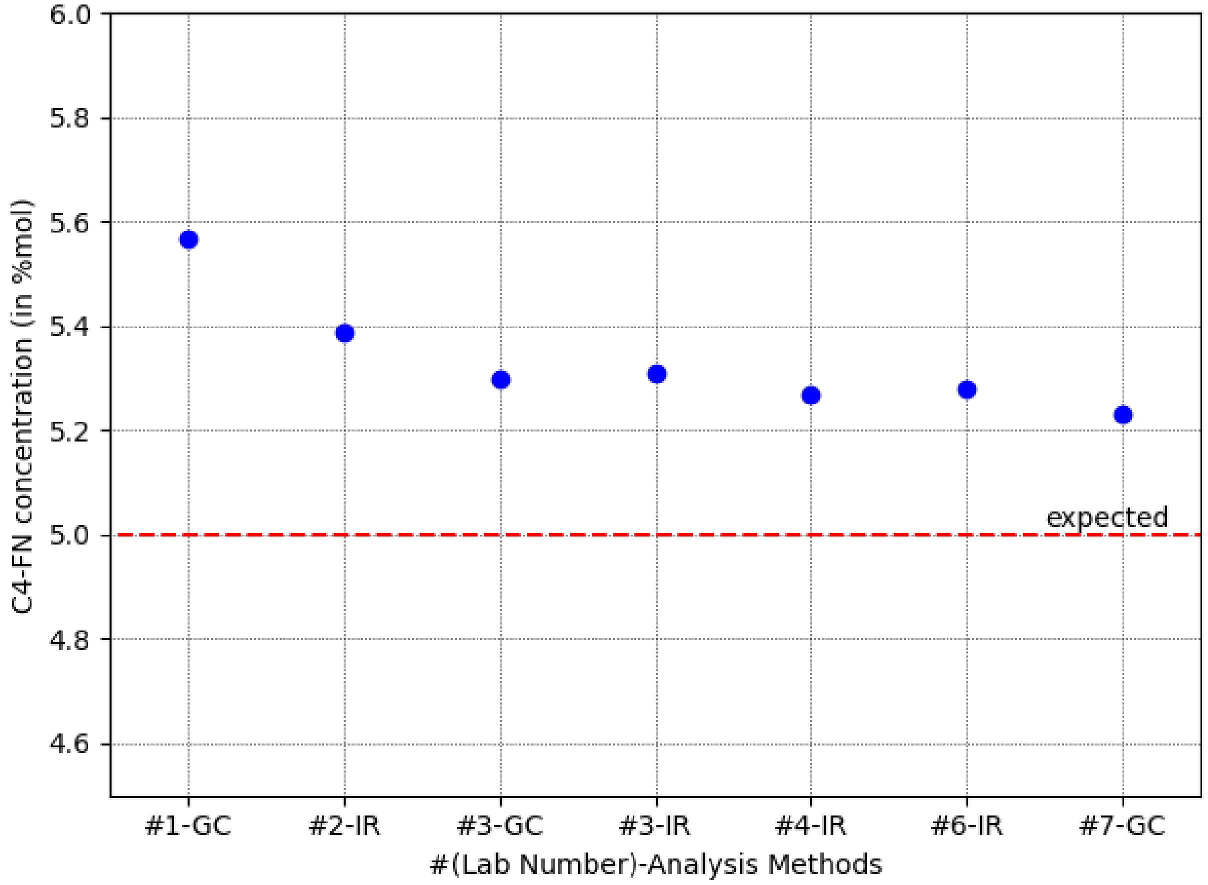
C4-FN / O_2 / CO_2 mixture (5% / 5% / 90%)



- reported values from 5.23 %mol to 5.57 %mol (within mutual uncertainty)
- but above target value and measurement before liquefaction

C5-FK / O_2 / CO_2 mixture (5.5% / 11.2% / 83.3%)

- Prepared with mass-flow controlled mixing device into large device
- Filled smaller sample bottles and transfer to labs

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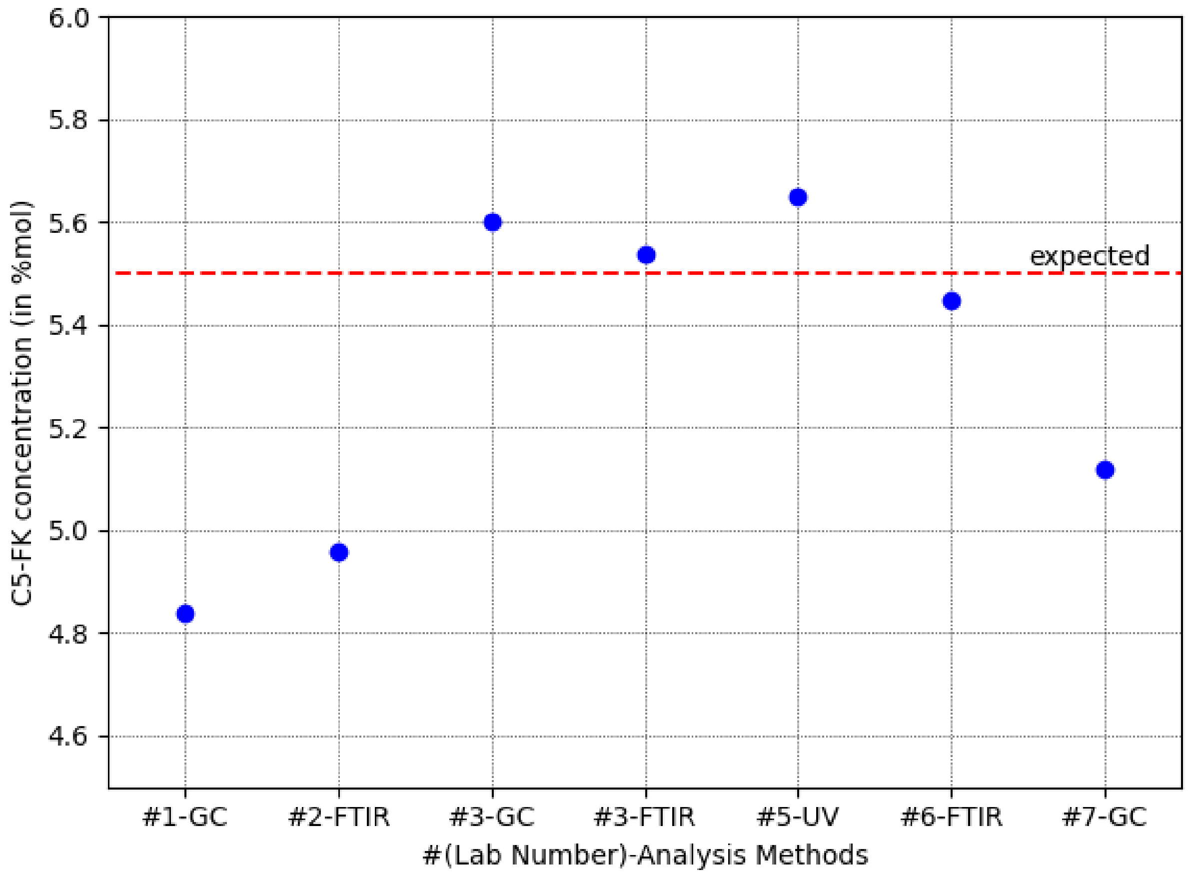
C5-FK / O_2 / CO_2 mixture (5.5% / 11.2% / 83.3%)



- reported values from 4.84 %mol to 5.65 %mol
- four out of seven within mutual uncertainty and around target value
- three significantly below others and below target

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Summary & Conclusion

«Part D: Gas Mixture Analysis»

- Gas analysis with ± 0.2 % abs. neither trivial nor consistently achievable
- No single root cause for deviations determined.
  Could be:
  - Calibration (no traceable calibration gases available)
  - Different analysis methods
  - Sample preparation and shipping

Summary and Conclusions

TB 849

- Comprehensive summary of know-how about fluorinated non-SF_6 gases
- One of the largest round robin breakdown test series was performed with 14 laboratories contributing.
- A set of test series was defined that lays the basis for qualification of new gases and can be taken as a guideline for future gas assessment.
- The experiments were designed separately for high-voltage and medium-voltage applications.
- Mixtures were selected based on proposals from manufactures to represent typical mixtures in application. A direct comparison of the novel gases was not aimed for, but comparison is made versus SF_6 only.

Summary and Conclusions

TB 849

- Despite extreme care, intra- and inter-laboratory reproducibility and comparability was not always possible to achieve (sometimes even for SF_6).
- C4-FN and C5-FK gas mixtures show the same principal discharge behavior as SF_6 (self-restoring gases for pure insulation purposes).
- HFO1234ze(E) and CF_3I are identified as non-self-restoring gases with degradation after breakdowns under the given conditions. An extra design margin is recommended to prevent flashovers during testing.
- A further round-robin test was conducted on gas analysis of C4-FN and C5-FK based gas mixtures
- Overall, an uncertainty of ±0.2% abs. seems to be not easily achievable, even under laboratory conditions

Electric performance of new non-SF6 gases and gas mixtures for gas-insulated systems

WG D1.67

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Thanks for your attention

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