



Material studies on RPC detectors operated with HFO/CO₂-based eco-friendly gas mixtures

Luca Quaglia^{1*}

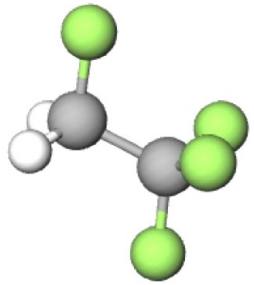
¹ETH Zurich, Università degli studi di Torino and INFN Torino

*Work funded by MSCA PF, EU grant number 101199027

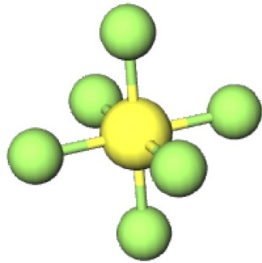
Outline

- RPCs and the issues with their gas mixture
 - HFO-1234ze as R134a substitute
- A complementary approach to the problem
 - Shift of focus from RPC performance to material studies
- Studies on a GIF++-aged RPC
 - Scanning Electron Microscope & X-ray diffraction studies
- Material compatibility studies
- Conclusions & outlook

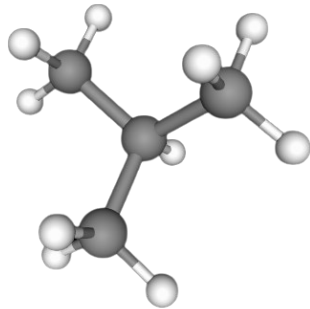
The currently employed gas mixture



90-95% $\text{C}_2\text{H}_2\text{F}_4$



0.3% SF_6



5-10% $\text{i-C}_4\text{H}_{10}$

+ 40% RH

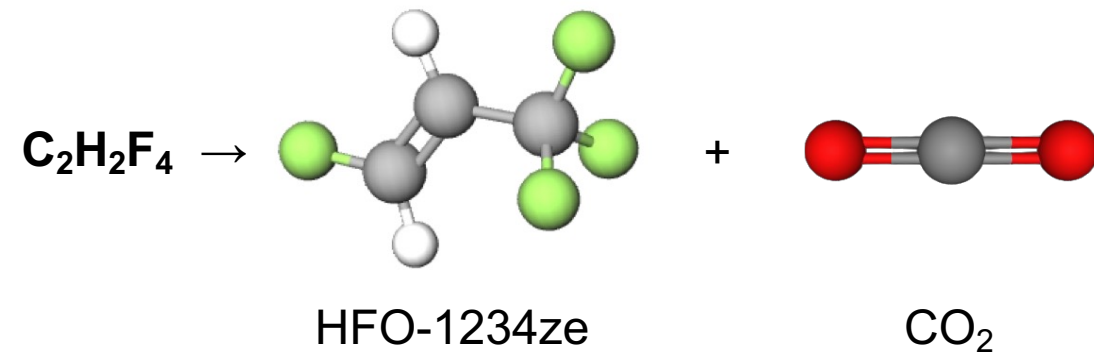
High-GWP mixture + phase out of F-gases

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Search for an alternative gas mixture for
RPCs

First effort of the RPC ECOGas@GIF++ collaboration:

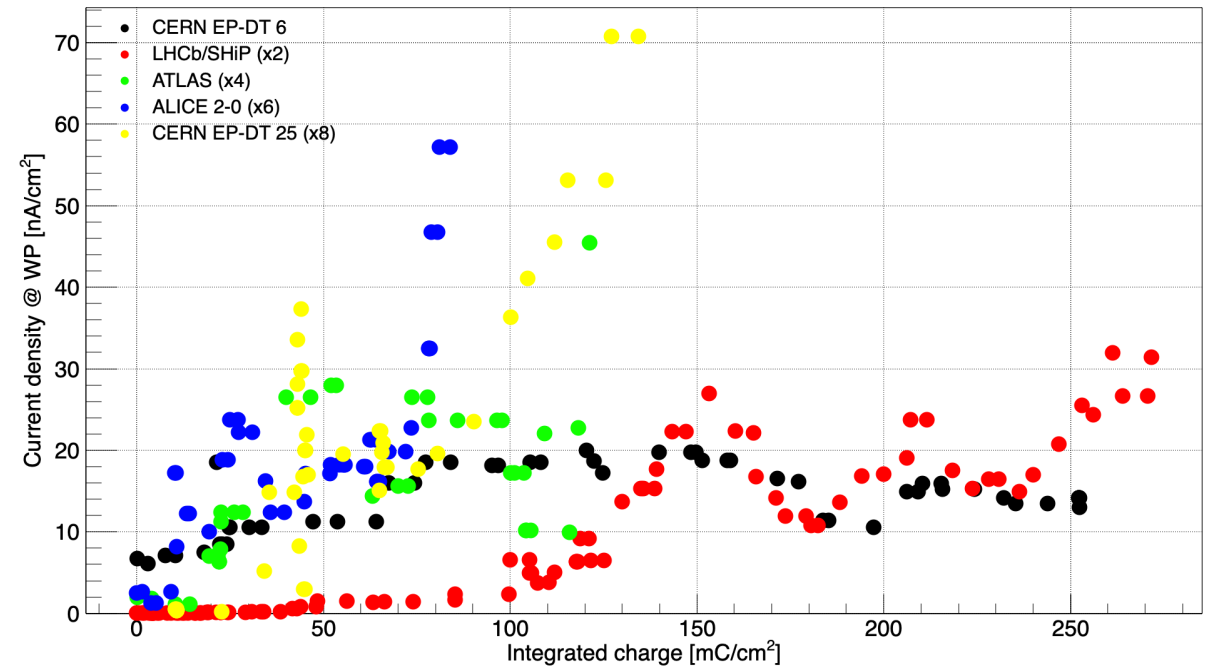
- Replace $\text{C}_2\text{H}_2\text{F}_4$ with HFO-1234ze + CO_2
- Study RPC performance with new gas mixtures*
- Study long-term detector stability*



*see [Marcello's talk](#)
for all the results

Aging results

- Several mixtures have been tested with muon beam [1,2,3]
 - Best candidate: **ECO2** (35% HFO + 60%CO₂ + 4% i-C₄H₁₀ + 1% SF₆) selected for long-term stability studies
- Long-term stability studied by the RPC ECOGas@GIF++ collaboration
 - Using the GIF++ ¹³⁷Cs source
 - No major performance degradation
 - **BUT** slight increase in absorbed dark current and shift in detector working point -> **not observed with the currently employed gas mixture and worth investigating to uncover root cause**



Dark current at working point for some of the RPCs used during the aging studies

Idea for a complementary approach

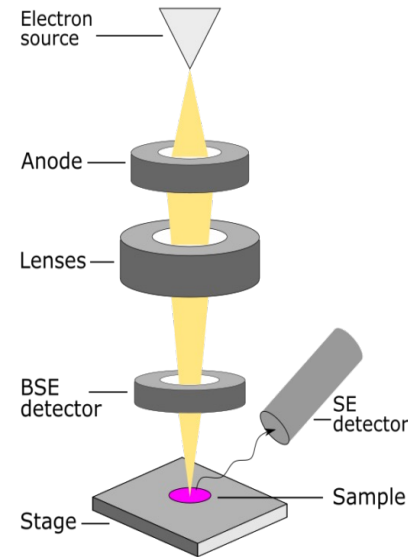
- No clear explanation for the observed behavior with the performance data currently available
- To gain more insights: try and decompose the aging phenomena in its “building blocks”
 1. Study HFO/CO₂ interaction with RPC materials after GIF++ exposure → *classic* aging
 2. Study material compatibility between HFO/CO₂ and RPC building materials → *chemical* aging
 3. Study aging effects induced by a different radiation source → *plasma-assisted* aging

Shift the research focus **from detector performance to material studies and their modification wrt non-aged materials** after being exposed to the new gases in different experimental conditions

Techniques used

1. Scanning Electron Microscope (SEM) + Energy Dispersive X-ray (EDX)

- To study elemental composition and get high magnification images of materials/defects



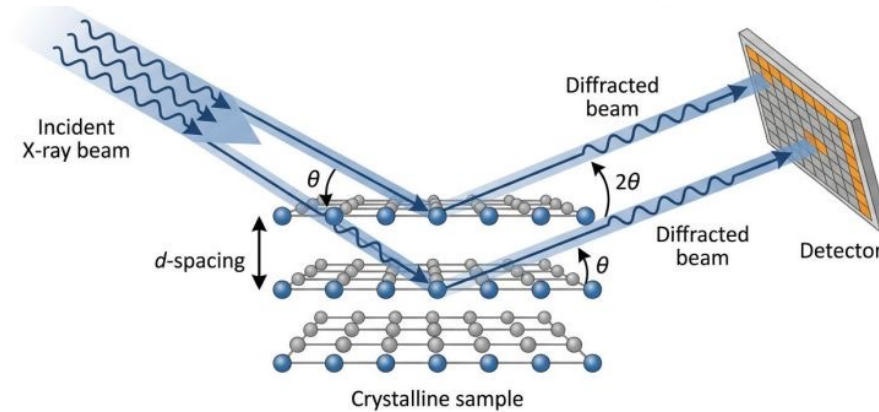
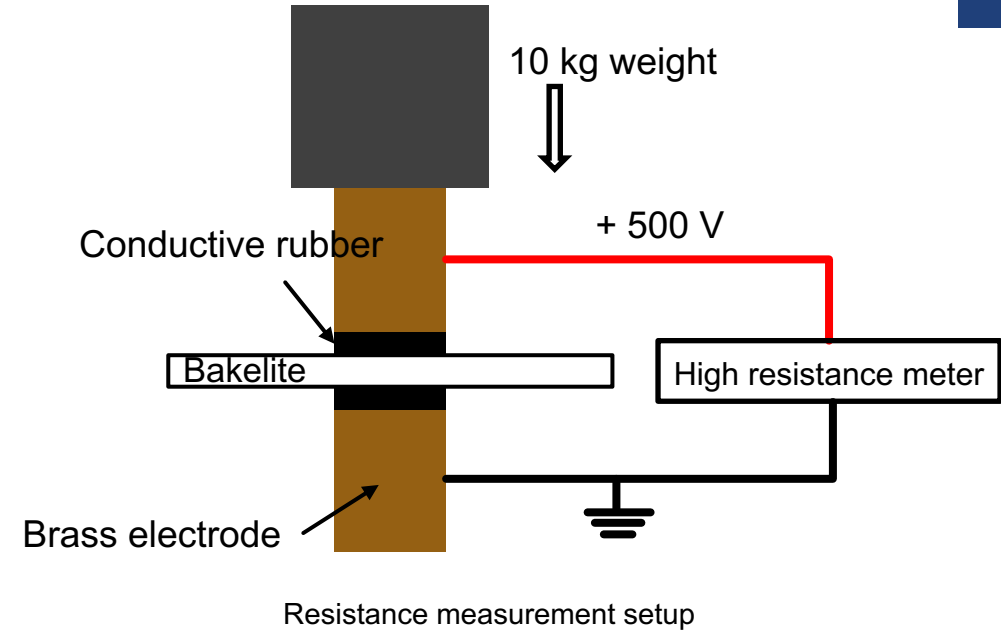
SEM scheme

2. X-ray Diffraction

- To study crystalline structure of defects

3. Resistivity measurements

- To study changes in electrical properties of the materials



XRD measurements scheme

Samples used

Material	Thickness (mm)	Description
Non-aged Bakelite	1.4	2025 production No linseed oil
	2	2021 production RPC With linseed oil
	2	< 2008 production No linseed oil
	2	< 2008 production With linseed oil
Aged Bakelite	2	GIF++ aged RPC 2021 production With linseed oil

**Interesting to compare
Bakelite from different
production rounds**

Recent samples

Oiled by the company

Oiling done in-house
with linseed oil from the
same company
producing it for industry

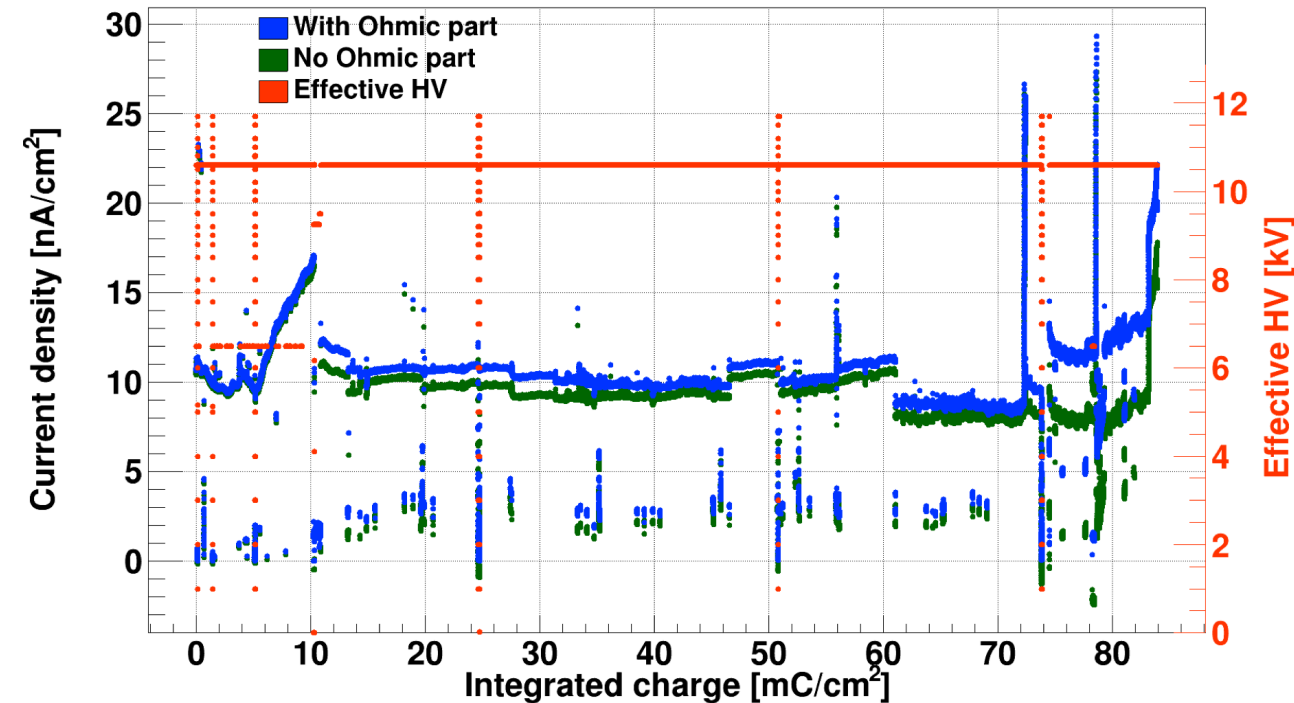
Oiled by the company

Studies on GIF++-aged RPC

ALICE RPC aged @ GIF++

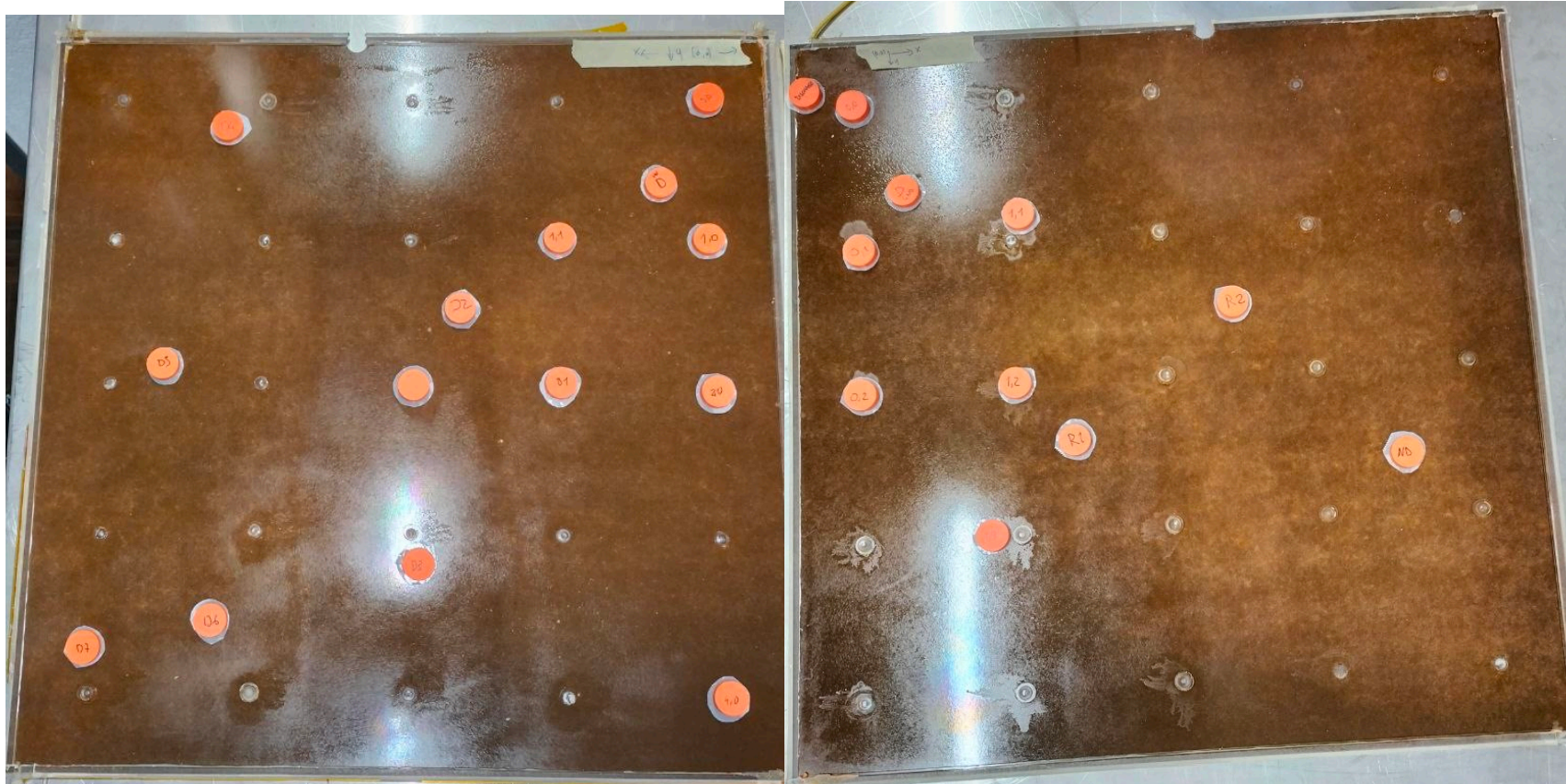
*Similar studies carried out on SHiP/LHCb RPC and preliminary results can be found [here](#)

- ALICE-like RPC prototype
 - 2 mm single gas gap + 2 mm Bakelite electrodes
 - Aged @ GIF++ with ECO2 gas mixture for ~1.5 years
 - **Total integrated charge ~ 90 mC/cm²**
 - Increase of absorbed current towards the end of the aging test
 - Detector was opened and internal surface analyzed: several defects were located* and studied with SEM and XRD



Trend of the absorbed current and applied HV during the aging campaign

Observed defects and their distribution



HV electrode with all identified defects

GND electrode with all identified defects

- Several defects located on both GND and HV (positive polarity) electrode
- Various morphology:
 - White *dust* deposits
 - Burns
 - Yellow deposits
 - Stains of missing linseed oil

SEM analysis of defects

HV electrode

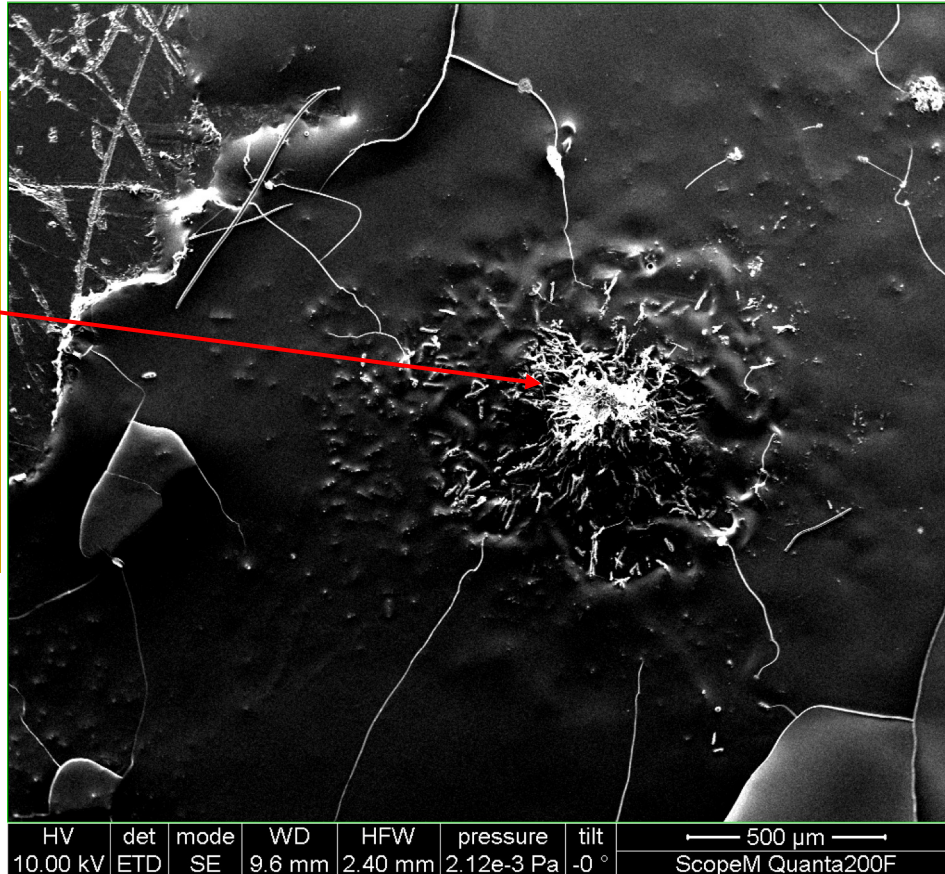


Bakelite sample from HV electrode

SEM analysis of defects



Bakelite sample from HV electrode



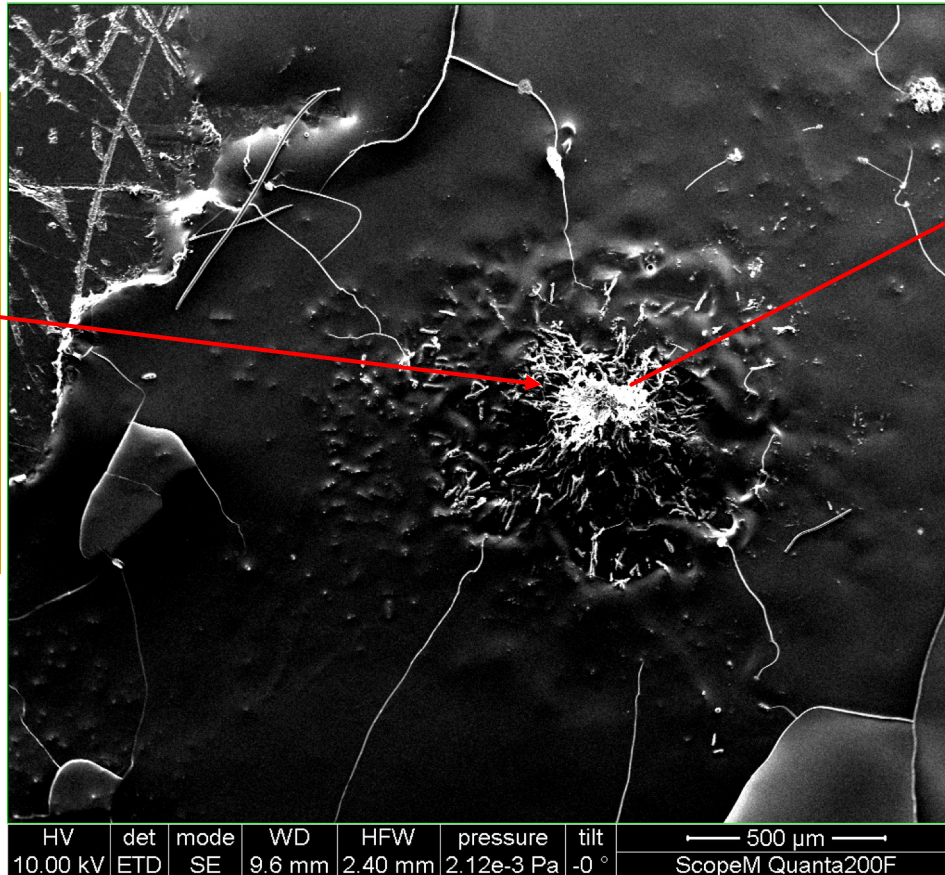
SEM image of "crater"-like defect

SEM analysis of defects

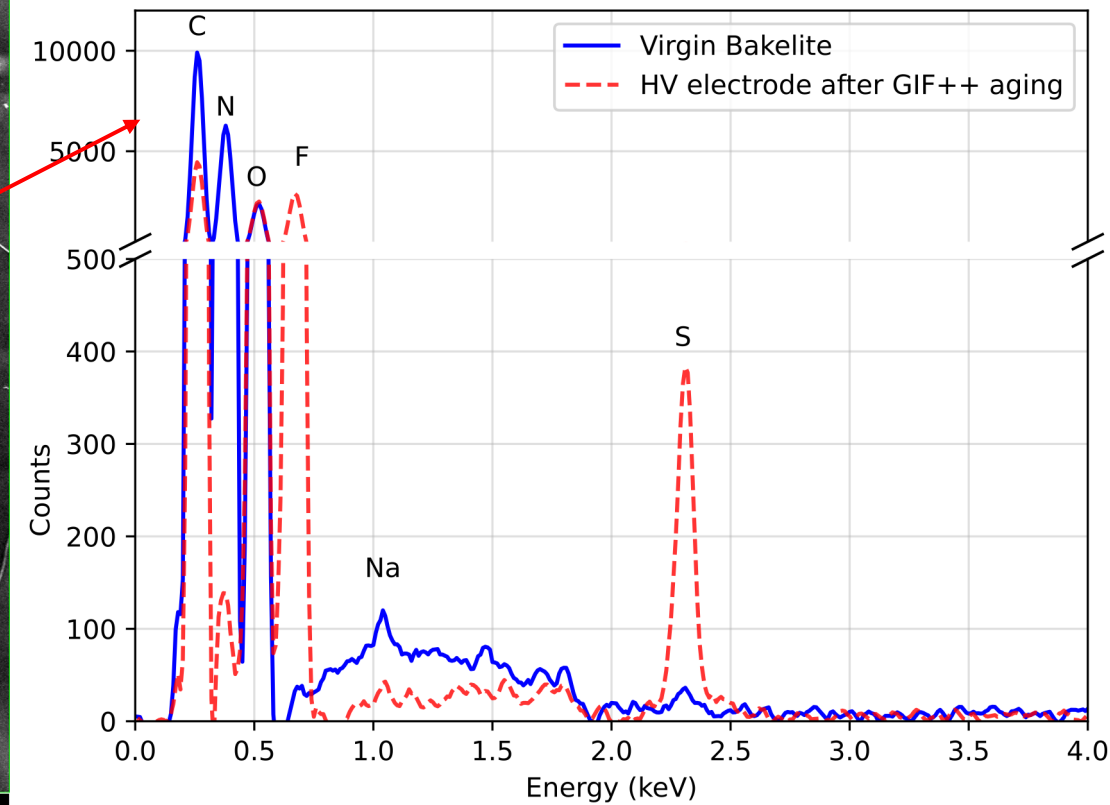
HV electrode



Bakelite sample from HV electrode



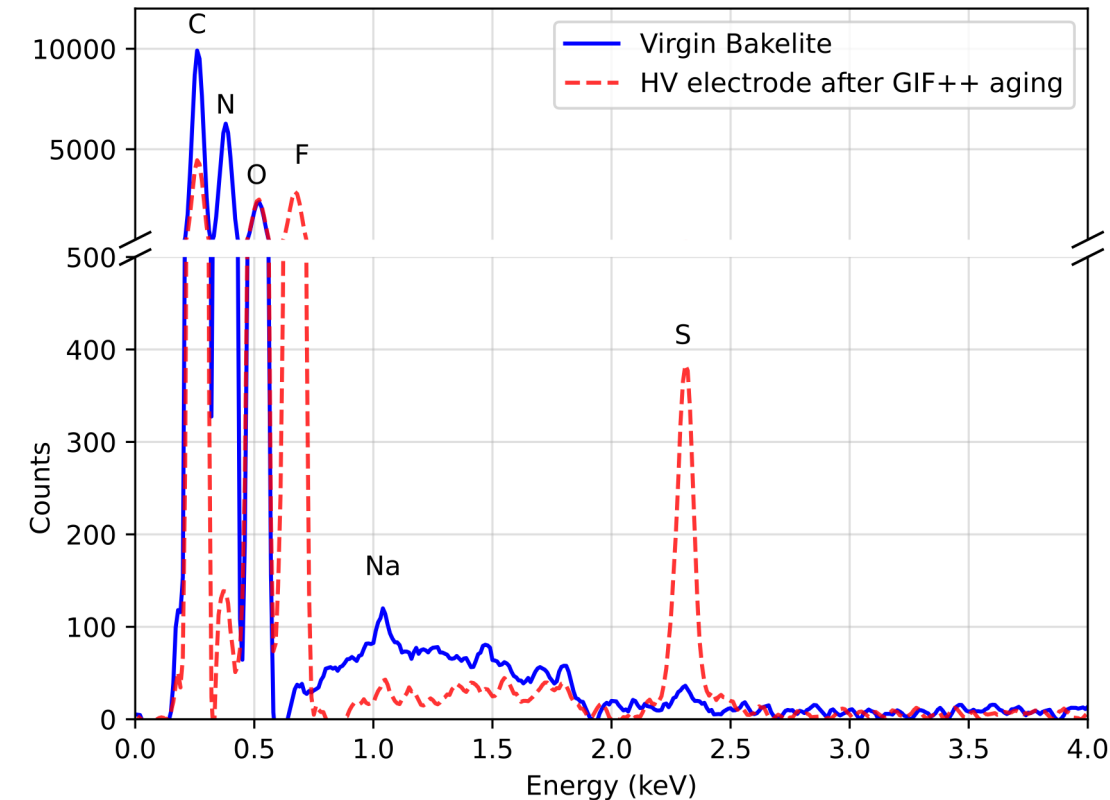
SEM image of "crater"-like defect



EDX spectrum of "crater"-like defect

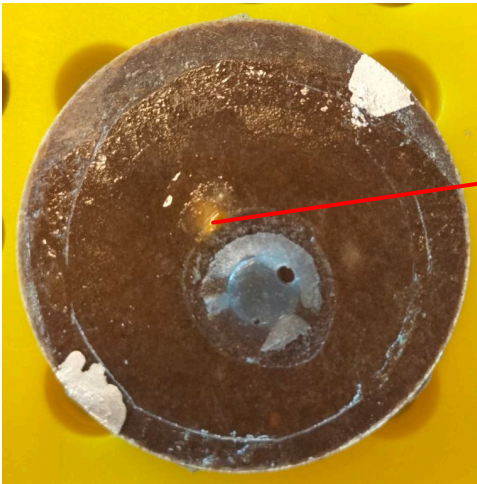
SEM analysis of defects

- **Carbon, Oxygen and Sodium** already present in virgin materials
- Appearance of **Fluorine** peak
 - From gas molecule dissociation
- Increase of **Sulphur** peak
 - Already present in trace amount in virgin material
 - Possibly from ionic conduction in Bakelite (?)

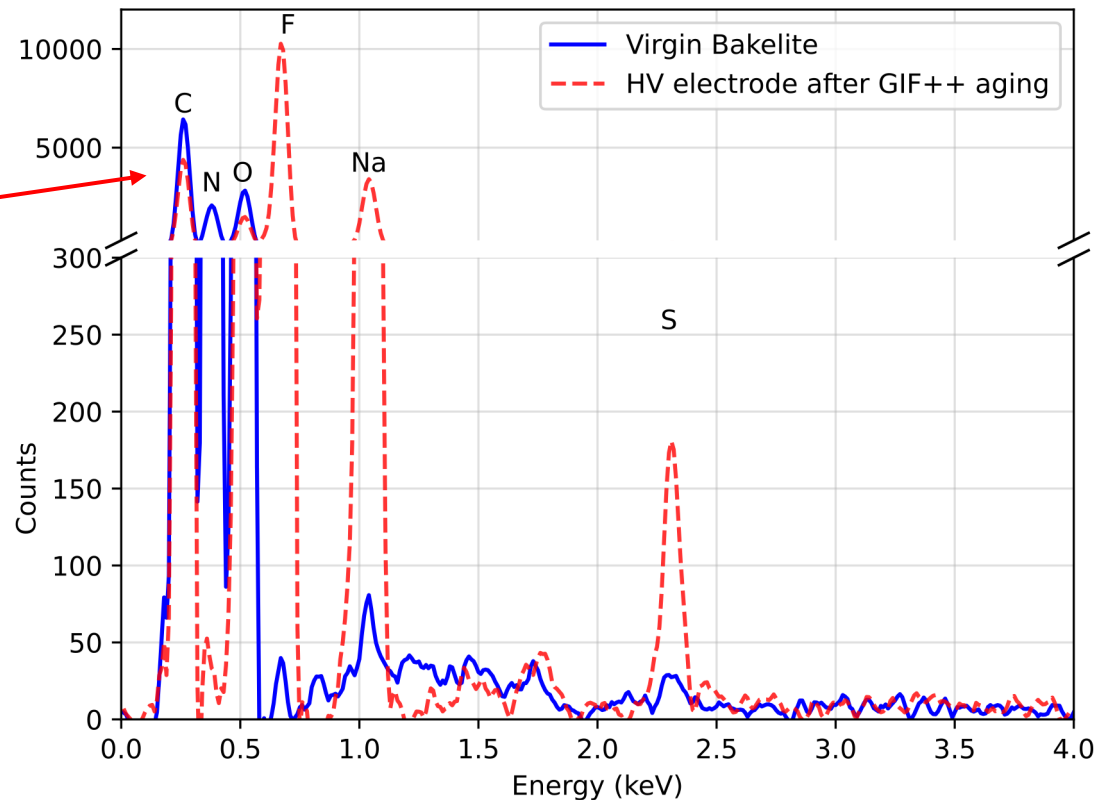


EDX spectrum of "crater"-like defect

SEM analysis of defects



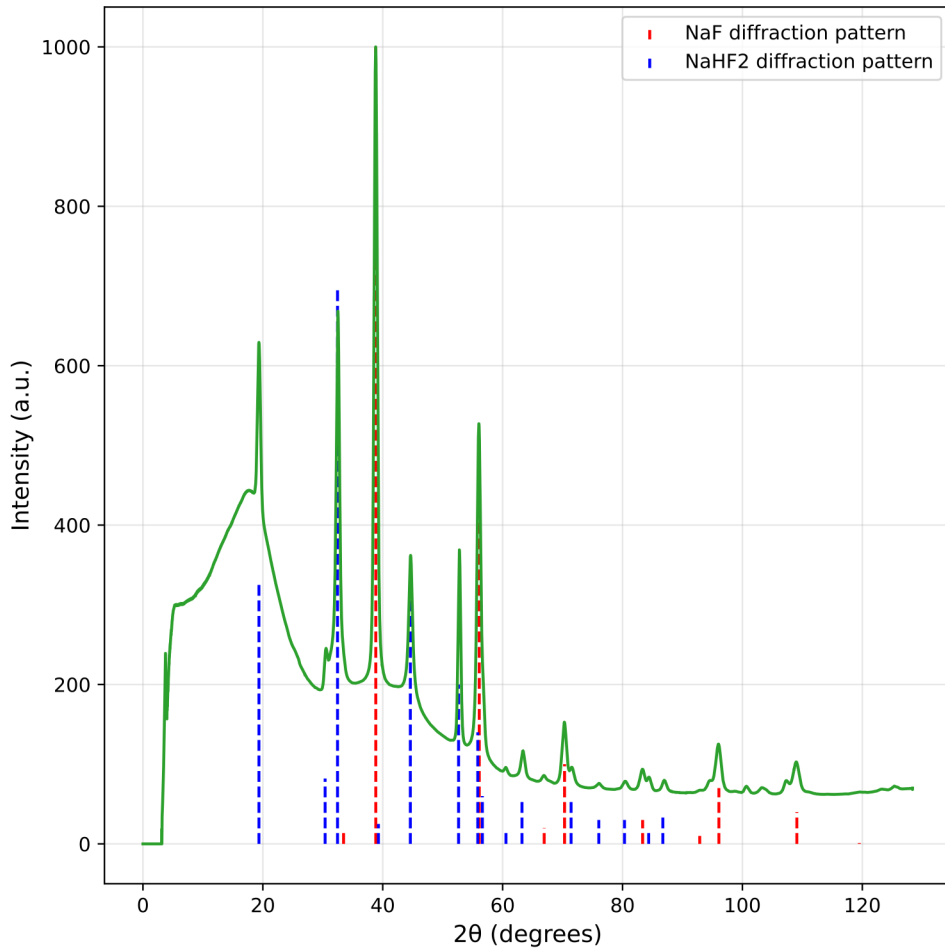
Bakelite sample from HV electrode



EDX spectrum of yellow dust deposit

- **Yellow dust** is richer in Na wrt virgin material
- **Fluorine** is always present
- **Sulphur** concentration depends on the location
- $\text{Na} + \text{F} = \text{NaF}$ crystals
→ XRD analyses

XRD analysis of defects



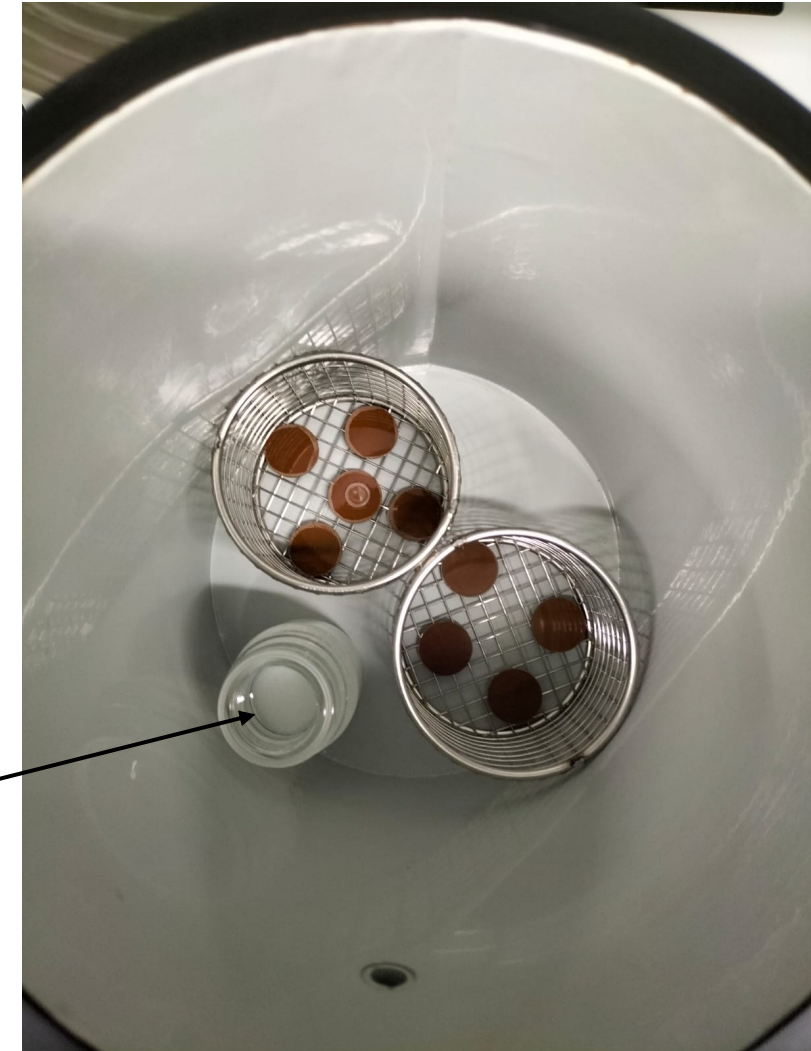
Experimental diffraction pattern of yellow dust (green) with NaF and NaHF₂ theoretical diffraction patterns (red and blue)

- X-ray diffraction analyses carried out on some samples from defected areas
- Yellow dust found to have crystalline structure, mixture of
 - **NaF**: sodium fluoride
 - **NaHF₂**: sodium bifluoride
 - Na and F have been observed with EDX (H is too light to be detected)
 - Consistent with Va'Vra's [\[1\]](#) model of ionic conduction in Bakelite
- Other defects have been found to be **non-crystalline**
 - FT-IR analyses scheduled soon for organic compounds identification

Material compatibility studies

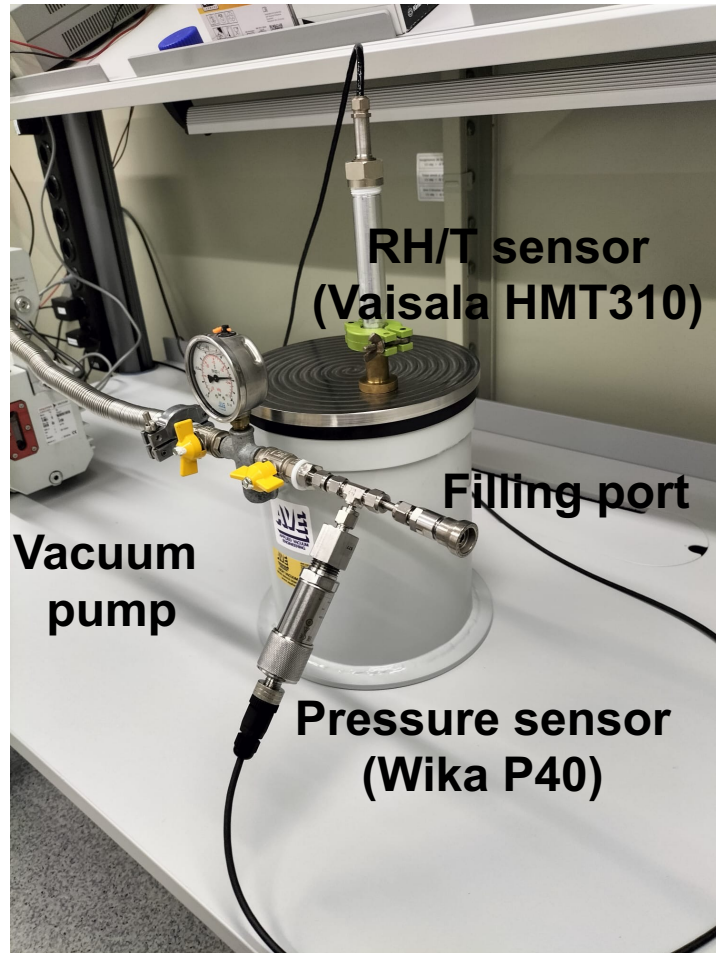
Material compatibility studies - 1

- **Goal:** investigate potential material modifications only due to bare chemical interaction with HFO/CO₂
- **Method:** long-term exposure of several Bakelite samples (from different productions) and spacers to a 60/40 CO₂/HFO mixture (similar to ECO2) in an enclosed vessel
- Vessel filled once to 800 mbar absolute pressure with desired mixture and internal conditions monitored for the whole duration of the exposure: **5.25 months**
 - 40% relative humidity -> obtained with saturated **NaI** salt solution [1,2]
- Repeat analyses before and after the exposure

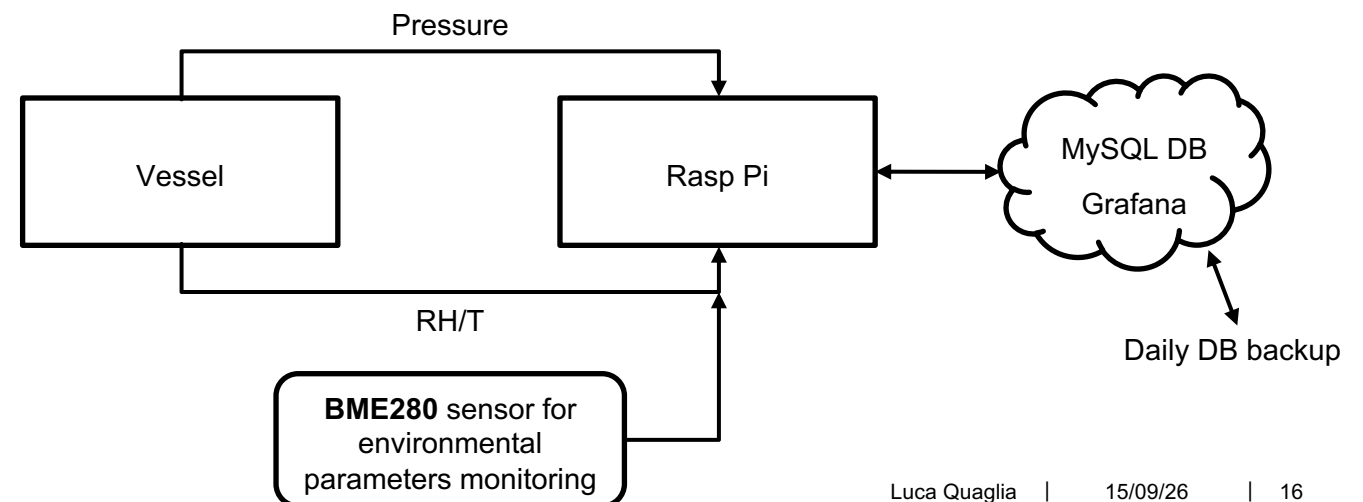
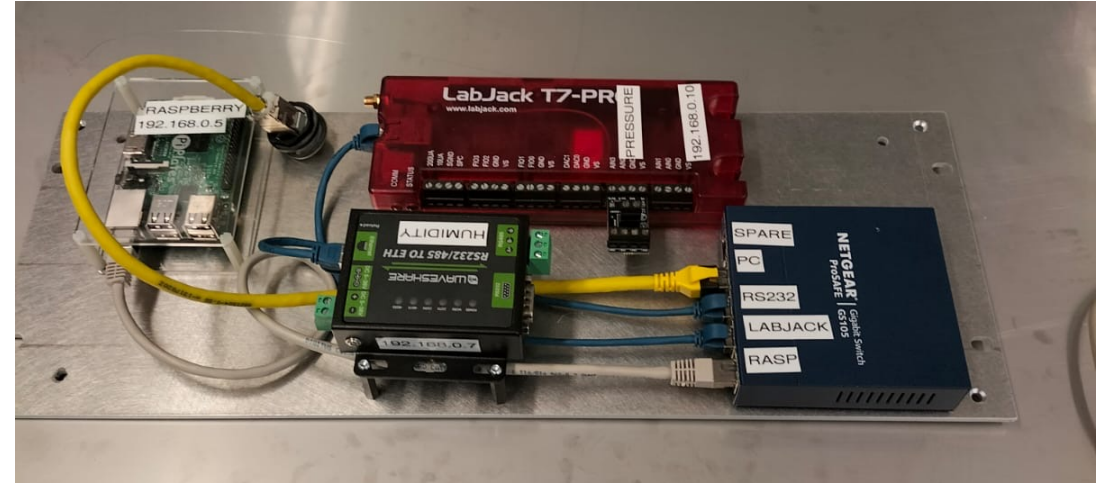


Bakelite samples exposed in the vessel

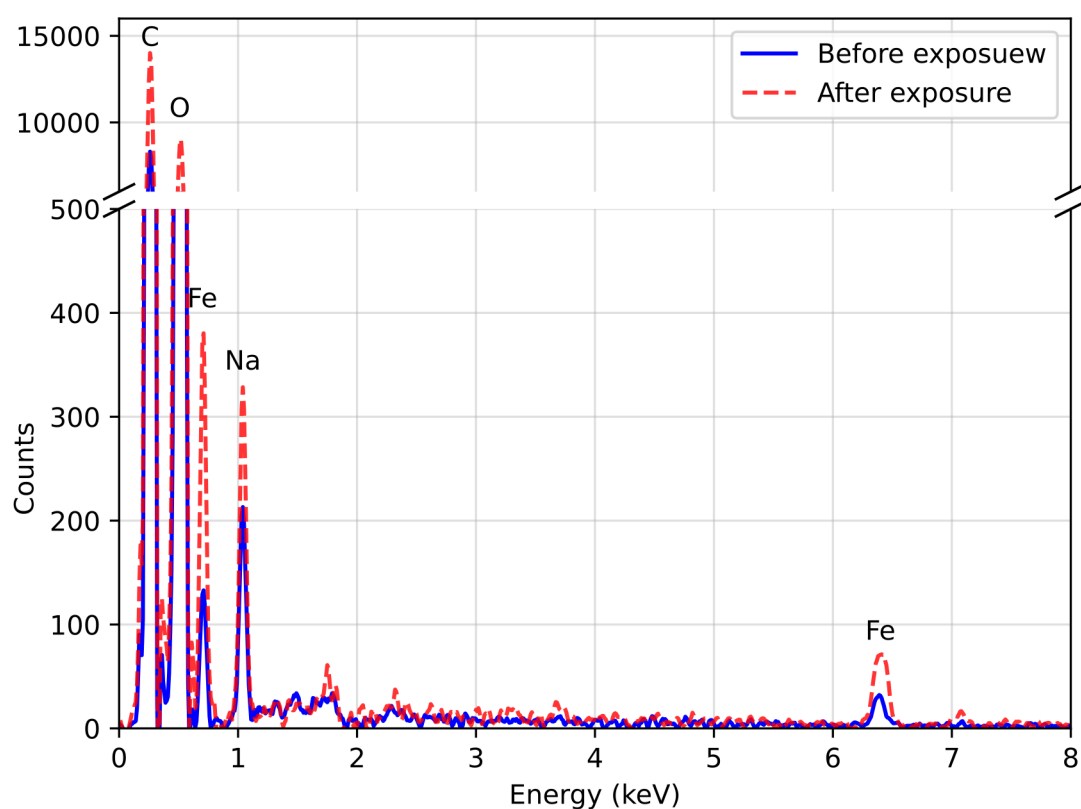
Setup for material compatibility studies - 2



Experimental setup



Material compatibility results - 1

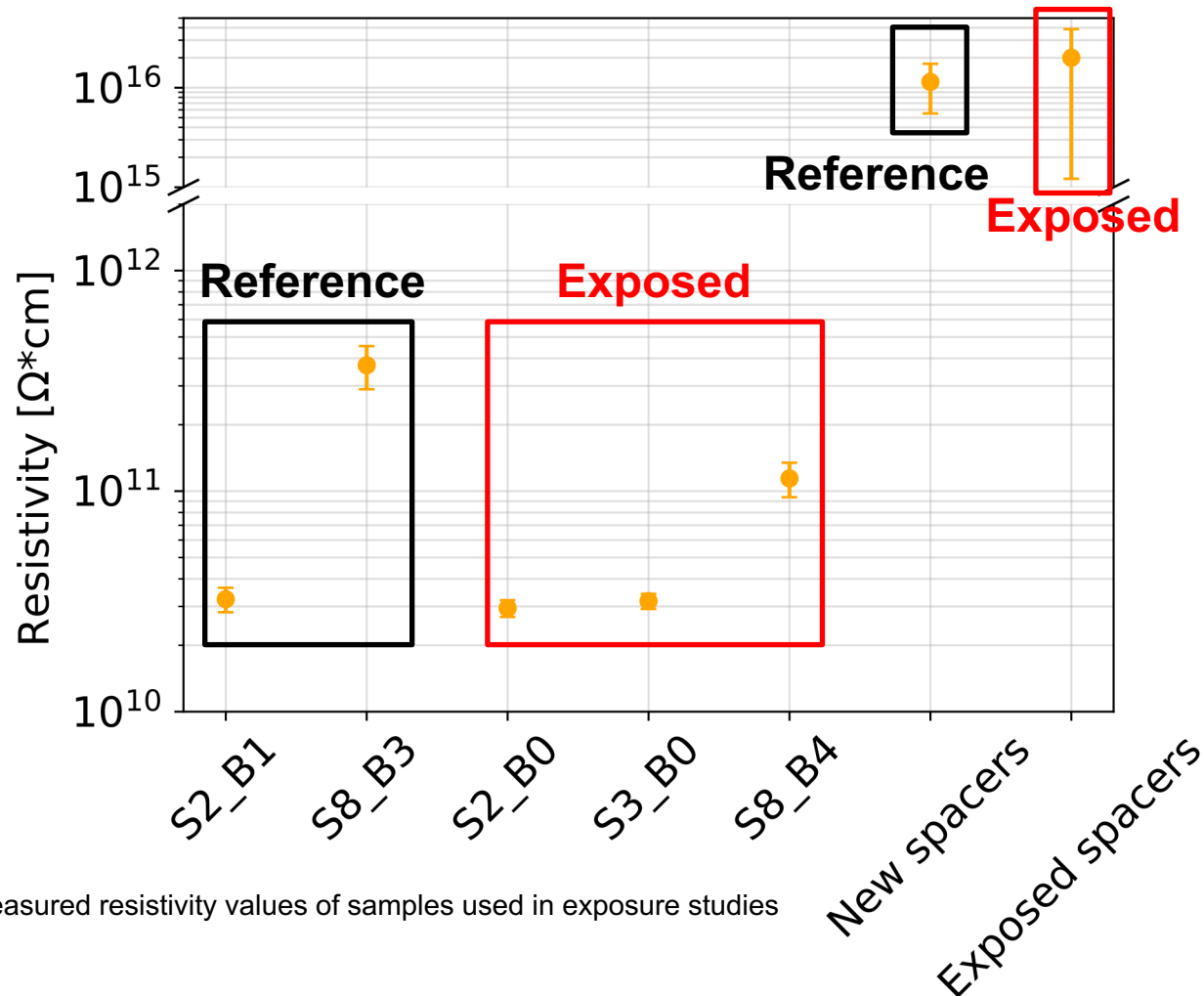


- Comparison of EDX spectra for samples **before** and **after** the exposure to the gases
- No appearance of new elements + similar concentrations before and after (see backup for full data) 😊
 - Element concentration estimated as ratio of area under its corresponding peak and sum of areas under all peaks

Material	Element	Abundance % (before exposure)	Abundance % (after exposure)
Old Bakelite no oil	C	56.12 ± 1.92	57.73 ± 1.86
	O	39.48 ± 1.47	38.45 ± 1.47
	Na	1.78 ± 0.14	1.93 ± 0.09
	Fe	3.42 ± 0.94	1.89 ± 0.23

- No change in material composition after the gas exposure
→ **Bare chemical interaction cannot explain the observed aging effects!**

Material compatibility results - 2



Measured resistivity values of samples used in exposure studies

- S2_B1 = old bakelite no oil (reference)
- S8_B3 = 2021 bakelite with oil (reference)
- S2_B0, S3_B0 = old bakelite, exposed
- S8_B4 = 2021 bakelite exposed
- Several measurements per sample
 - Uncertainty given by combination of statistical and instrumental uncertainties
- **No significant changes in the measured resistivity values after the material exposure**

Conclusions

- Detailed material studies of RPC building materials from different productions
- Studies on GIF++-exposed RPC
 - Visual changes to the materials (burns, white and yellow deposits)
 - EDX analyses have shown increase in F, Na and S concentration in the defects
 - XRD analyses showed the presence of NaF and NaHF₂ crystals within the defects
 - Similar features observed in RPCs operated with STD gas mixture [\[1\]](#), **effects not totally imputable to HFO-1234ze**
- Completed exposure to HFO/CO₂ gas mixture for material compatibility studies
 - SEM/EDX analyses and resistance measurements have shown no changes of materials before and after the gas exposure
 - Simple gas-material interaction cannot explain the aging effects observed in the GIF++-aged RPC
 - **Paper in publication with results**



Thanks a lot for your attention!

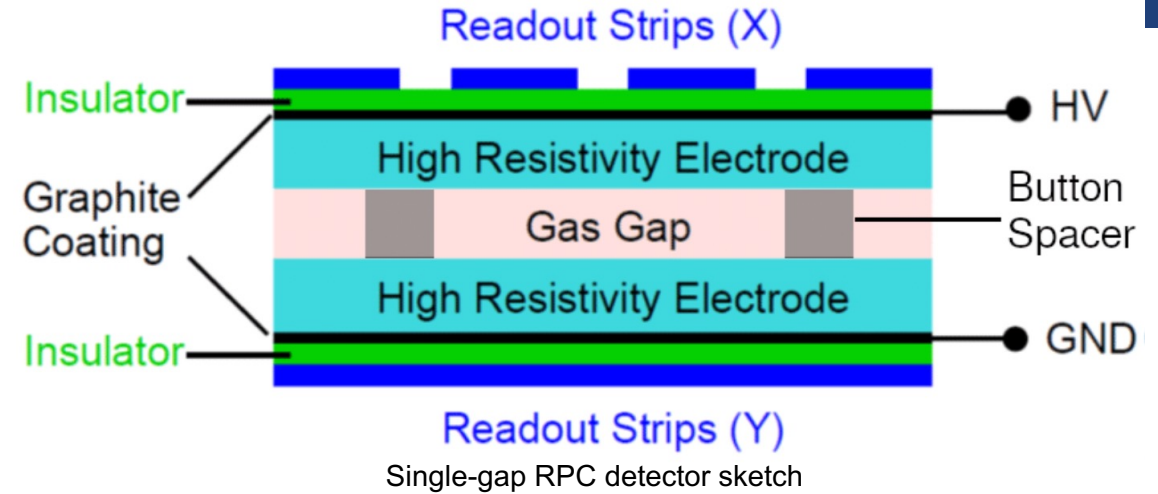
Future plans

- Design and build setup for [plasma-assisted aging studies](#)
 - Dielectric barrier discharge (DBD) technique chosen
 - Increased-speed aging with plasma, possible with different gases
To disentangle “chemical” from “mechanical” effects
- Perform FT-IR analyses on non crystalline defects
- Try to model the observed aging effects starting from Va’Vra’s model of ionic conduction in Bakelite

Backup

Resistive Plate Chambers

- Particle detector employed for muon detection [1]
- **Electrodes**
 - Bakelite or glass
- **Button spacers and frame**
 - Polycarbonate plastic
- **Gas mixture**
 - Delicate balance, key to ensure proper functioning
- **Bakelite electrodes**
 - Polymerized linseed oil layer to smooth out surface imperfections



RPC inner electrode view

Project steps

This talk

1. Characterize brand new detector building materials from different productions
 - i. Obtain **reference** data
2. Study materials from an RPC exposed to the GIF++ irradiation
 - i. Compare to **virgin materials** and study results of *aging effects*
3. Perform material compatibility studies
 - i. Expose virgin materials to new gas (no radiation/HV)
 - ii. Compare results after exposure to **virgin + GIF++-aged** materials
 - iii. If material features change only following gas exposure -> **part of the aging can be attributed to pure chemical incompatibility**
4. Perform plasma-assisted aging studies with HFO/CO₂
 - i. Similar to GIF++ aging conditions with a different source of radiation
 - ii. Faster charge accumulation wrt current aging studies
 - iii. Study the dependence of aging effects from charge accumulation speed and different radiation source

Upcoming

Sample used and preparation

Bakelite (50x50 cm²)



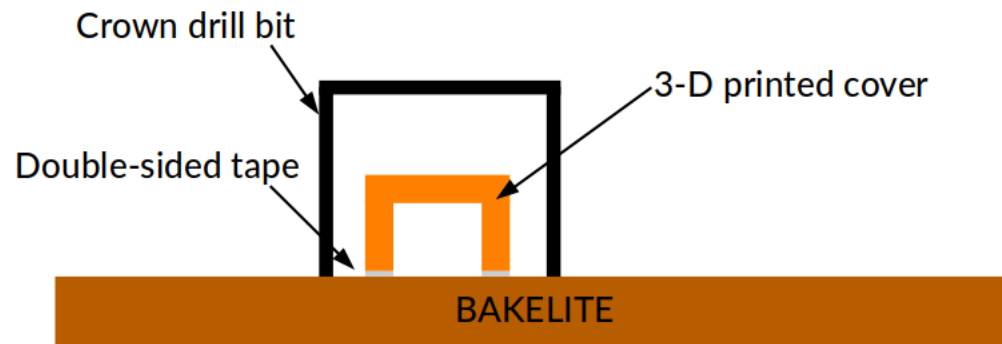
Cut to smaller size (12x12 cm²)



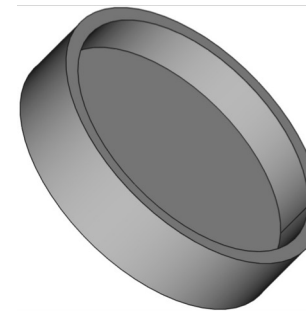
Cut 1" circles (SEM sample holder size)
Cut 10 cm circles for resistivity measurements



[3D printed cover](#) to protect from dust + crown drill bit



Side view of sample cutting procedure



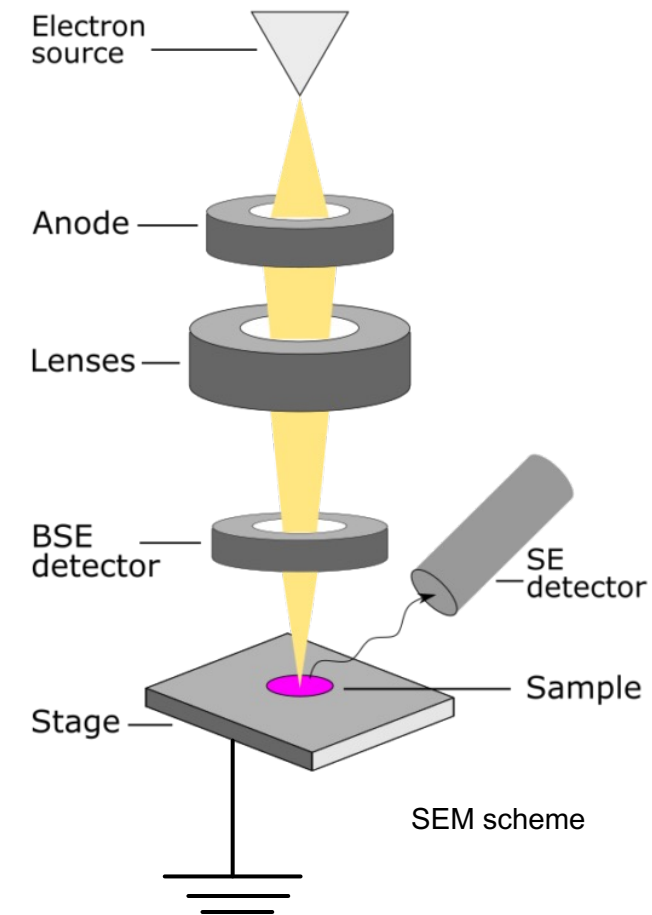
Custom dust cover



Cutting Bakelite samples

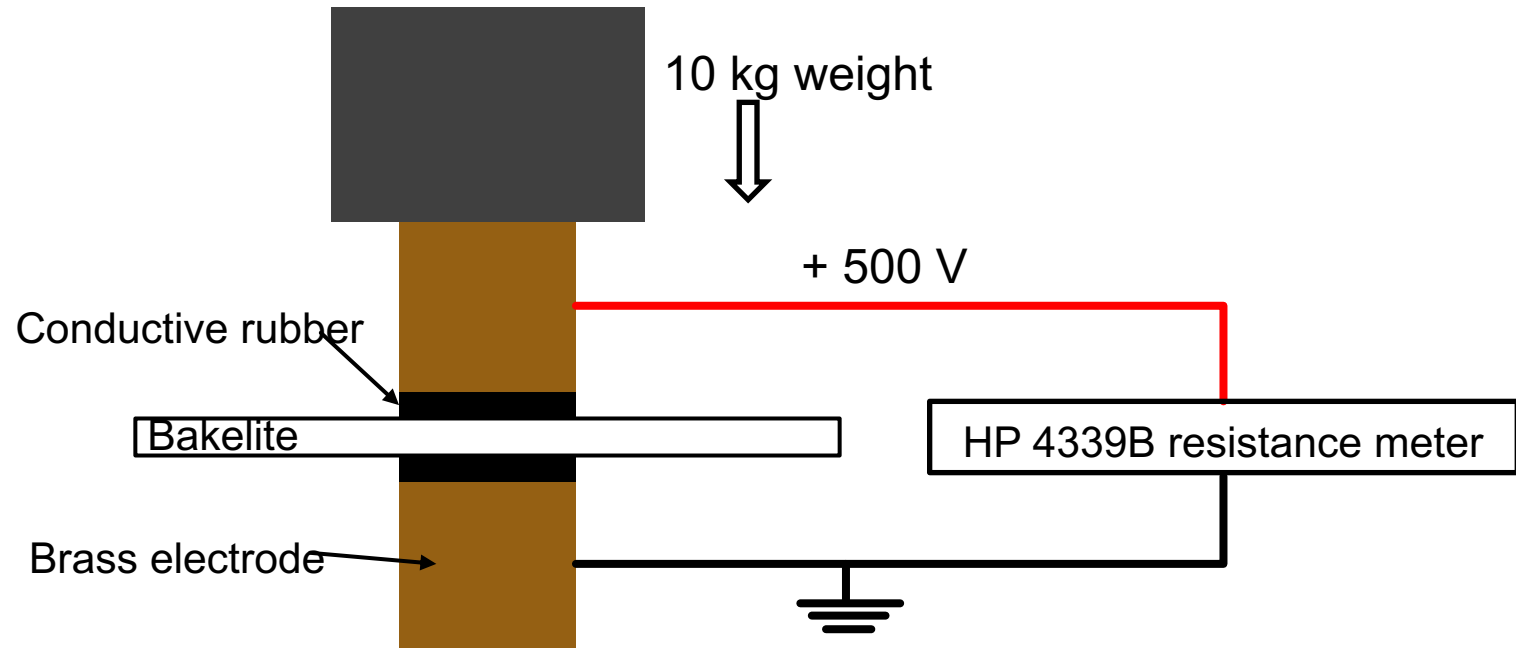
SEM data-taking

- Electron beam to probe the material
 - Resistive materials cause charge accumulation on the sample
 - Sputter 10 nm carbon coating + connect the carbon to sample mount (grounded)
- **SE** = secondary electrons, emitted from the material (low energy ~50 eV)
 - Topography info
- **BSE** = back-scattered electrons, electrons from the beam reflected from the sample (high energy)
 - Material contrast (strong correlation with atomic number)
- **EDX** = energy-dispersive X-ray (**only for elements heavier than Li**)
 - Identify atomic composition of the material
 - Exploiting the characteristic X-ray emission of atoms



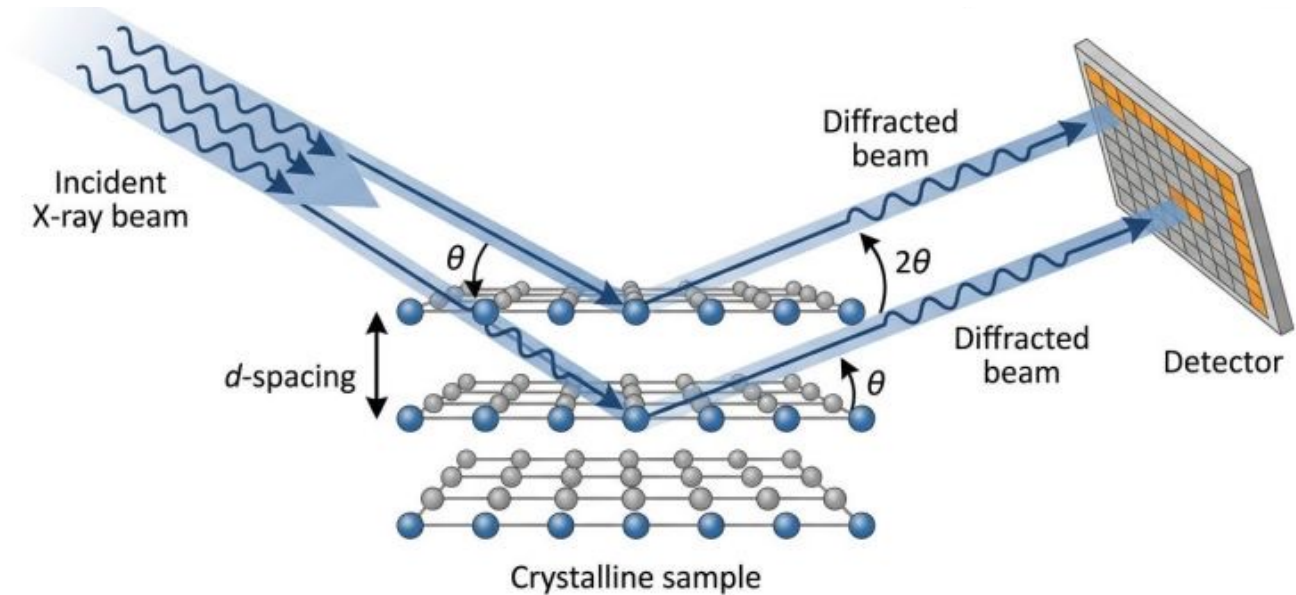
DC bulk resistivity measurements

- [HP 4339B high resistance meter](#)
- DC voltage up to 1000 V
 - Measure of the absorbed current
 - Resistance determination
 - 10 kg weight applied on the samples to grant electrical contact
- Conductive rubber and brass electrodes to contact the material
- Low noise leads to connect electrodes to high-resistance meter
- 0.6% accuracy up to $10^{16} \Omega$

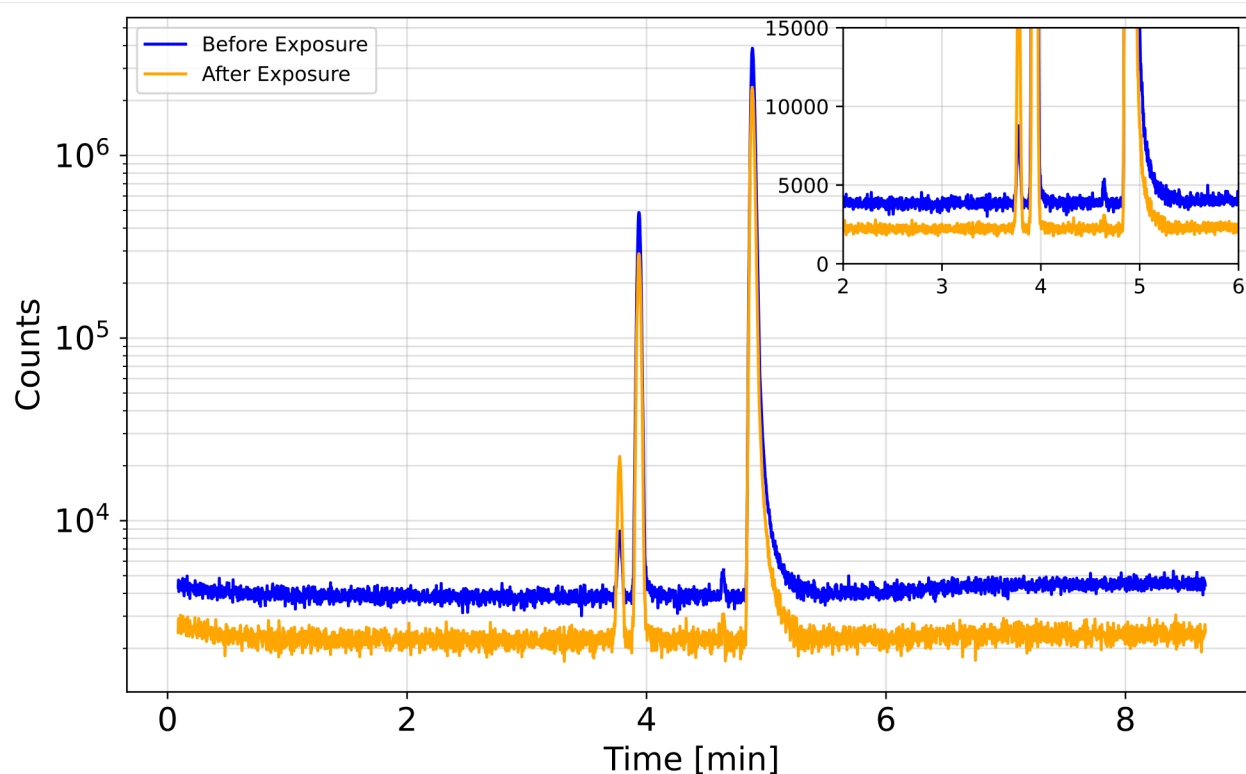


XRD measurements

- It uses the scattering of X-rays by crystal planes to identify crystal structures, phase composition, and atomic spacing based on constructive interference
- Bragg's Law ($2d \sin(\theta) = n \cdot \lambda$) explains that constructive interference occurs when the path difference of scattered X-rays equals a whole number (n) of wavelengths (λ) and d is the distance between parallel planes of atoms in a crystal lattice



GC/MS analyses during material exposure studies



Chromatogram comparison before and after exposure to the gases

- Two samples of gas extracted from the vessel
 - **Start of exposure**
 - **End of exposure**
- GC/MS analyses did not show the appearance of any new elements
 - Simple chemical interaction does not lead to impurity formation
- Area ratio before and after the exposure gives an estimate of element concentrations

Element	Area % (before exposure)	Area % (after exposure)
Air	0.120	0.729
CO ₂	10.481	10.122
Impurity (HFO-1234yf)	0.023	0.017
HFO-1234ze	89.375	89.132

Element concentration from mass spectrum analysis

Full list of results for EDX analyses after material exposure

Material	Element	Abundance % (before exposure)	Abundance % (after exposure)
Old Bakelite no oil	C	56.12 ± 1.92	57.73 ± 1.86
	O	39.48 ± 1.47	38.45 ± 1.47
	Na	1.78 ± 0.14	1.93 ± 0.09
	Fe	3.42 ± 0.94	1.89 ± 0.23
Old Bakelite with oil	C	70.65 ± 2.03	76.25 ± 0.34
	O	28.19 ± 2.04	22.34 ± 0.32
	Na	0.59 ± 0.01	0.94 ± 0.08
New Bakelite with oil	C	58.77 ± 1.43	59.25 ± 1.14
	O	23.87 ± 1.06	25.07 ± 1.14
	Na	1.19 ± 0.09	1.05 ± 0.09
	N	17.22 ± 2.3	12.85 ± 1.77
	F	0.58 ± 0.05	0.34 ± 0.04
	S	0.55 ± 0.04	0.58 ± 0.07

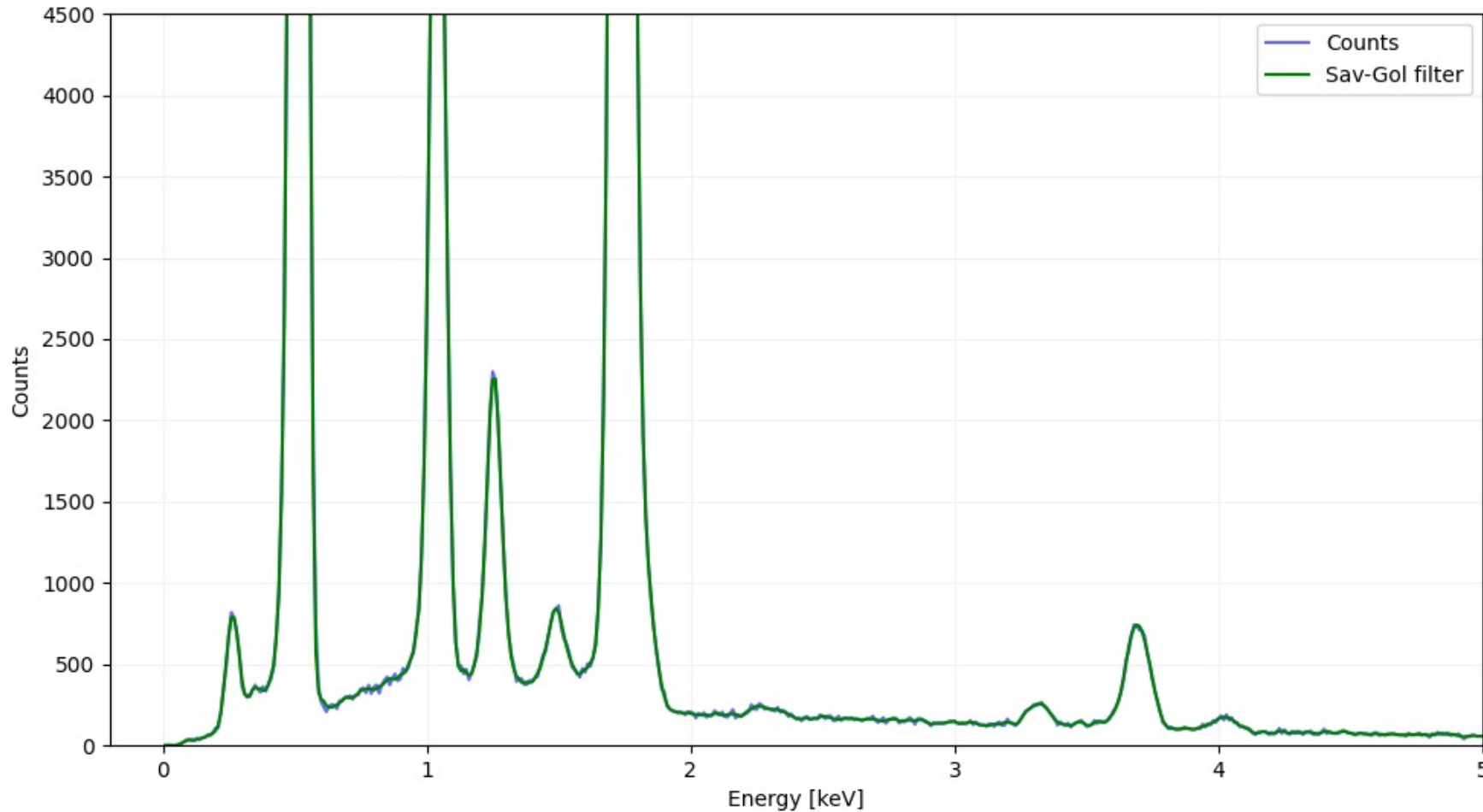
Elemental composition of the samples before and after the exposure

- Elemental composition before and after gas exposure for all the tested materials
- No significant change in composition for any material
- Statistical error calculated thanks to multiple EDX spectra collected in several locations on the samples

- Carbon, Oxygen and Nitrogen = basic constituent of Bakelite
- Sodium (Na) = from NaOH used as activator in Bakelite production
- Iron (Fe) in old Bakelite no oil = residual in paper manufacturing process [\[1,2\]](#)
- Fluorine (F) in new Bakelite with oil = from RPC usage with cosmic rays
- Sulphur (S) = present as trace element in Bakelite production

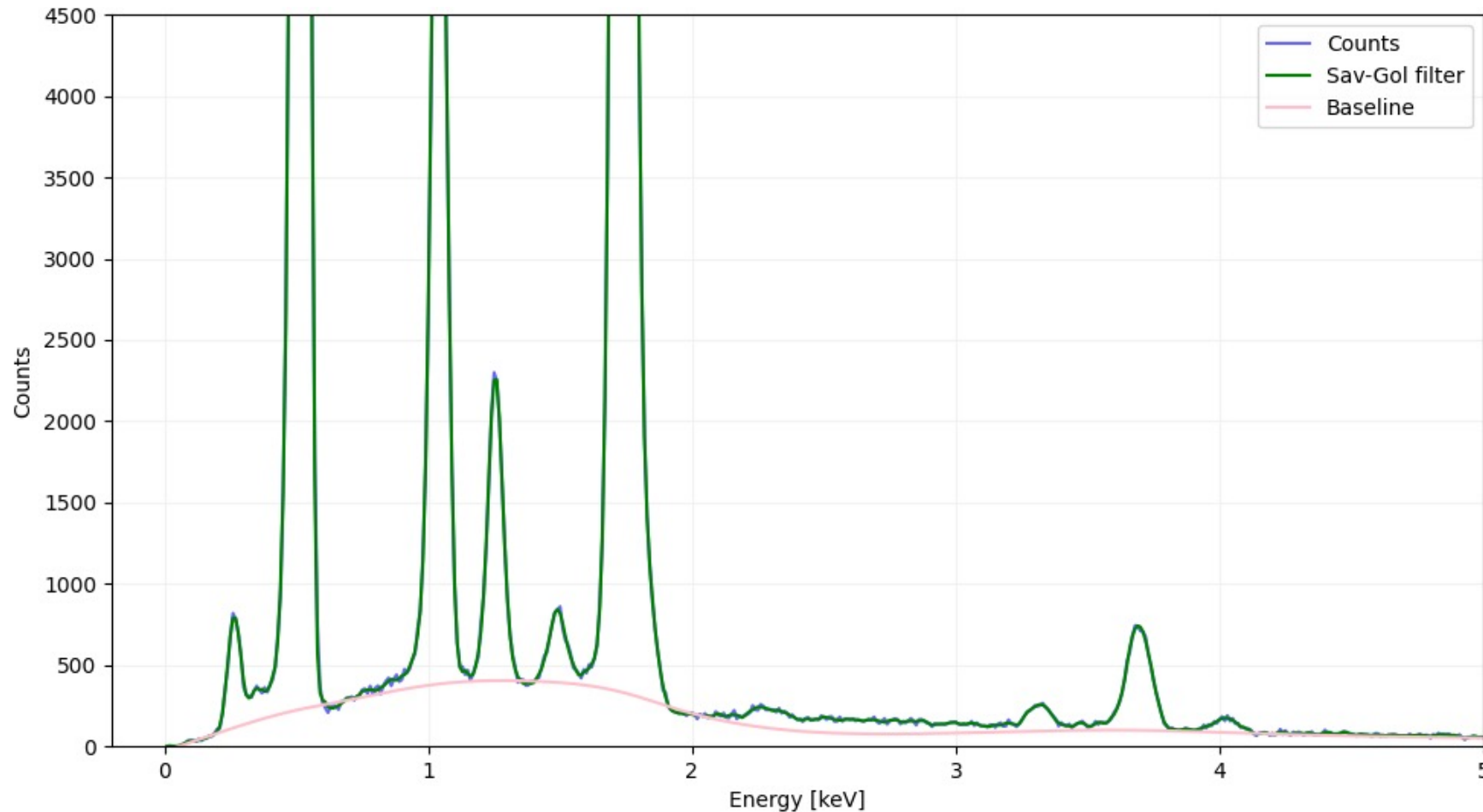
Element concentration from mass spectrum analysis

EDX data processing



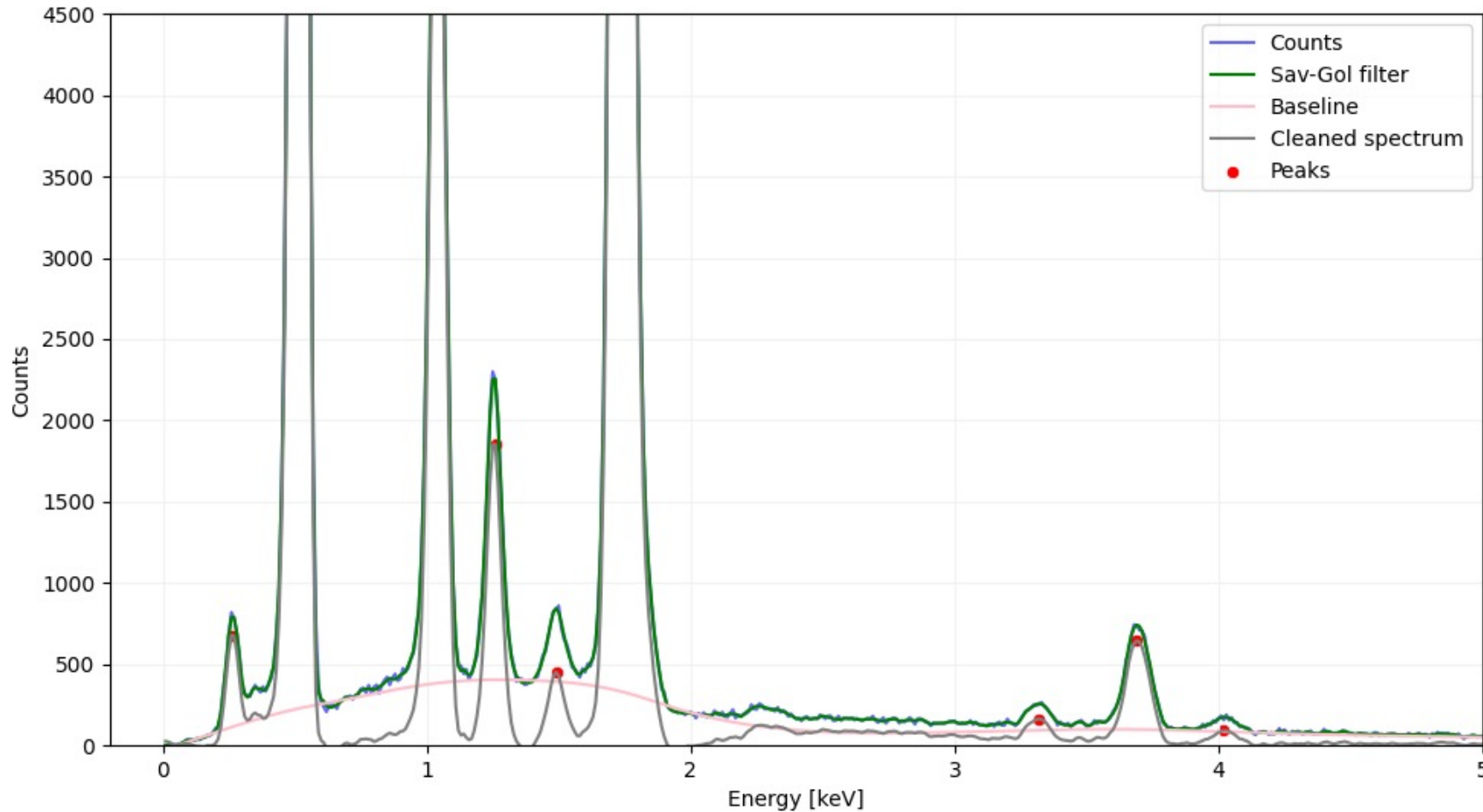
- Apply [Savitzky-Golay filter](#) to smooth out the data
- Window = 15 points
- Order of polynomial = 6

EDX data processing



- Estimate baseline with [Asymmetric Least Square \(ALS\)](#) smoothing method
- Parameters have been found by hand but there is room for improvement

EDX data processing



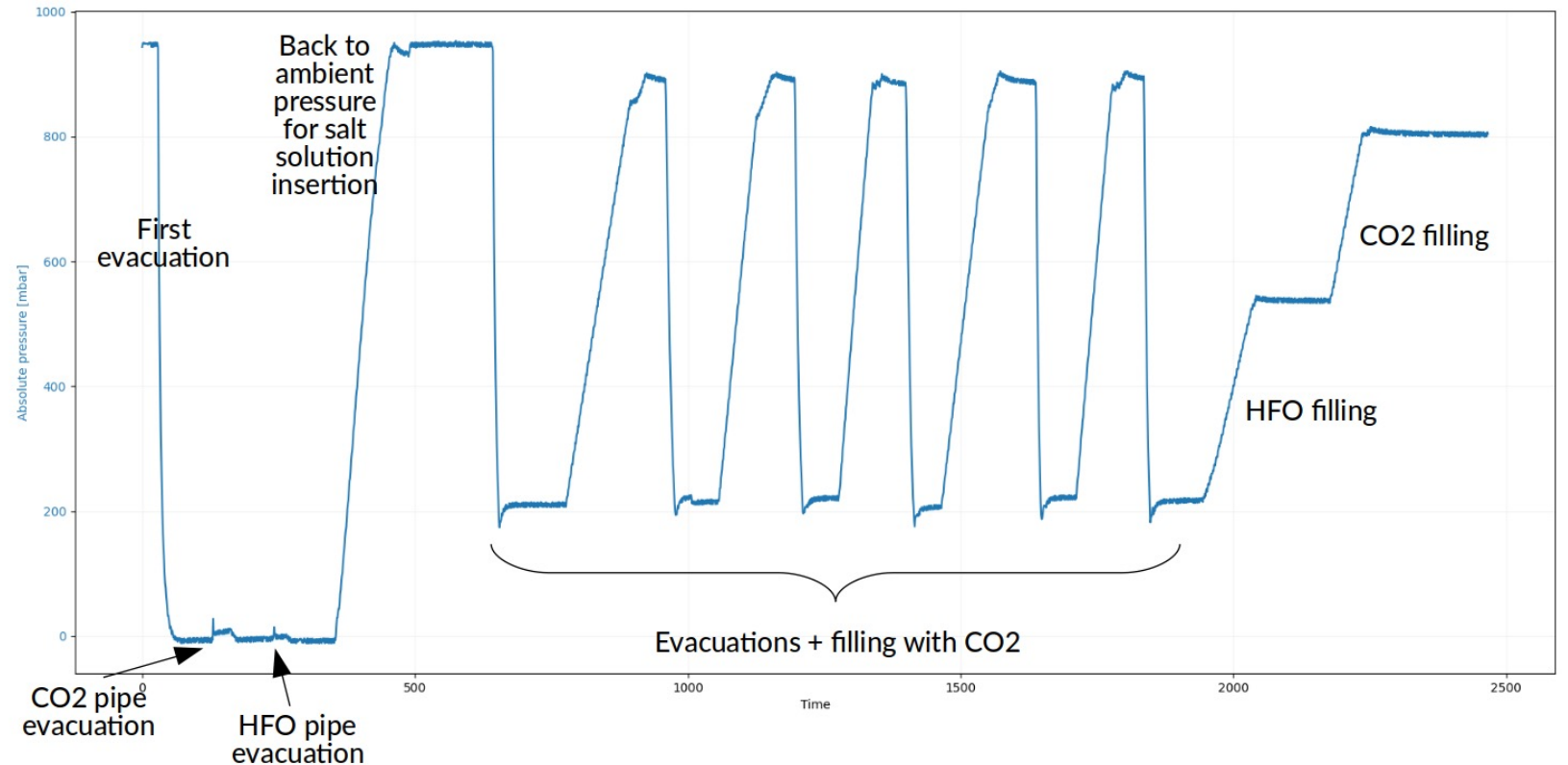
- Subtract baseline from spectrum and find actual peaks
- Peaks are known from [tables of X-ray emission](#)
- Semi-quantitative analysis possible

Vessel filling procedure

Salt solution contains water, boils in vacuum

Filling done in steps:

1. Evacuate vessel without salt solution and evacuate pipes
2. Bring back vessel to ambient pressure and insert salt solution
3. Evacuate down to 200 mbar
4. Fill with CO₂ up to 800 mbar
5. Evacuate and repeat 5 times to dilute and remove the residual air from the vessel
6. Fill with HFO
7. Finish CO₂ fill up to 800 mbar



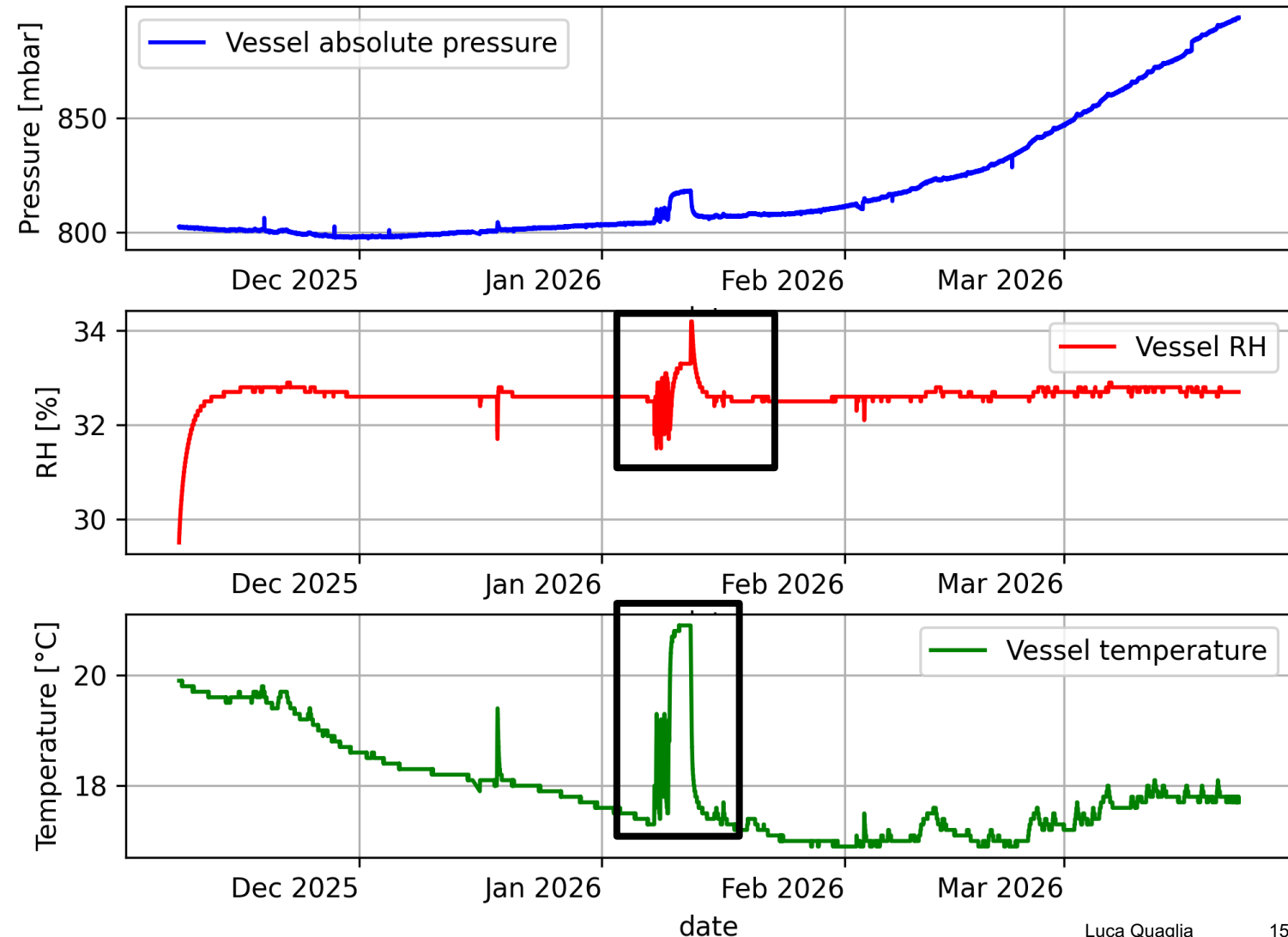
11-2025 -> 03/2026

Vessel conditions monitoring during exposure

Pressure shows increasing trend
-> Tightness of the vessel checked before starting and was ok

Stable RH values
-> 40% measured with air in the vessel
-> Lower reading of the sensor due to [CO₂ presence in the gas](#)

Temperature in the room is not controlled
-> Tried to warm up the lab with a small heater but idea abandoned due to humidity instability



Trend of environmental parameters within the vessel

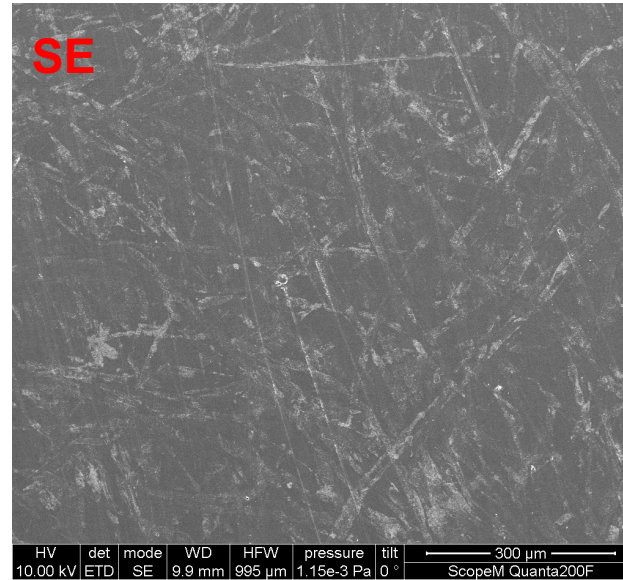
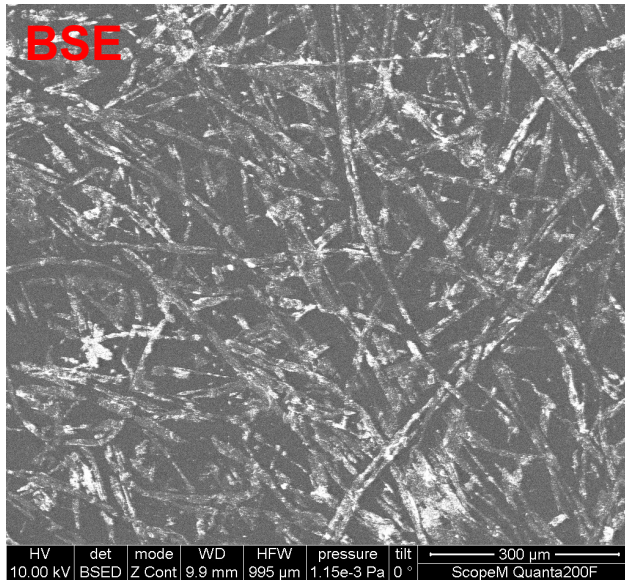
Luca Quaglia

15/09/26

| B10

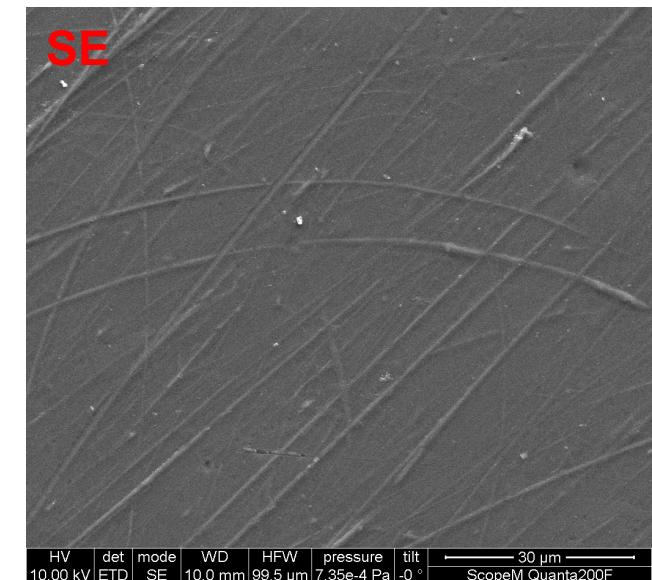
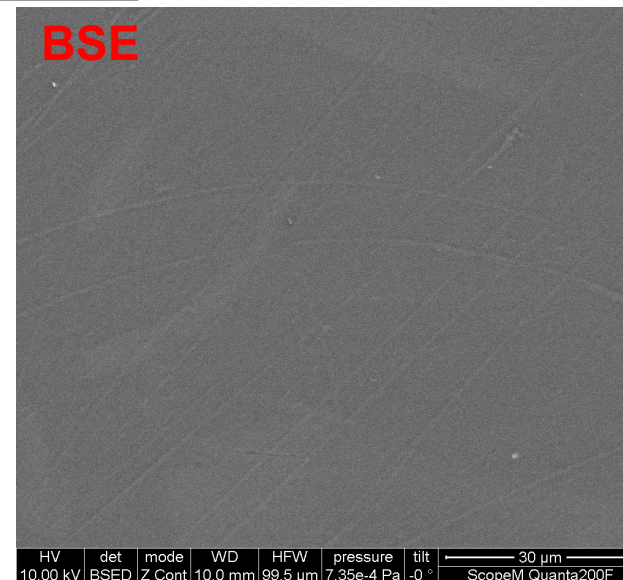
Bakelite
Top view

SEM results for virgin materials - 1



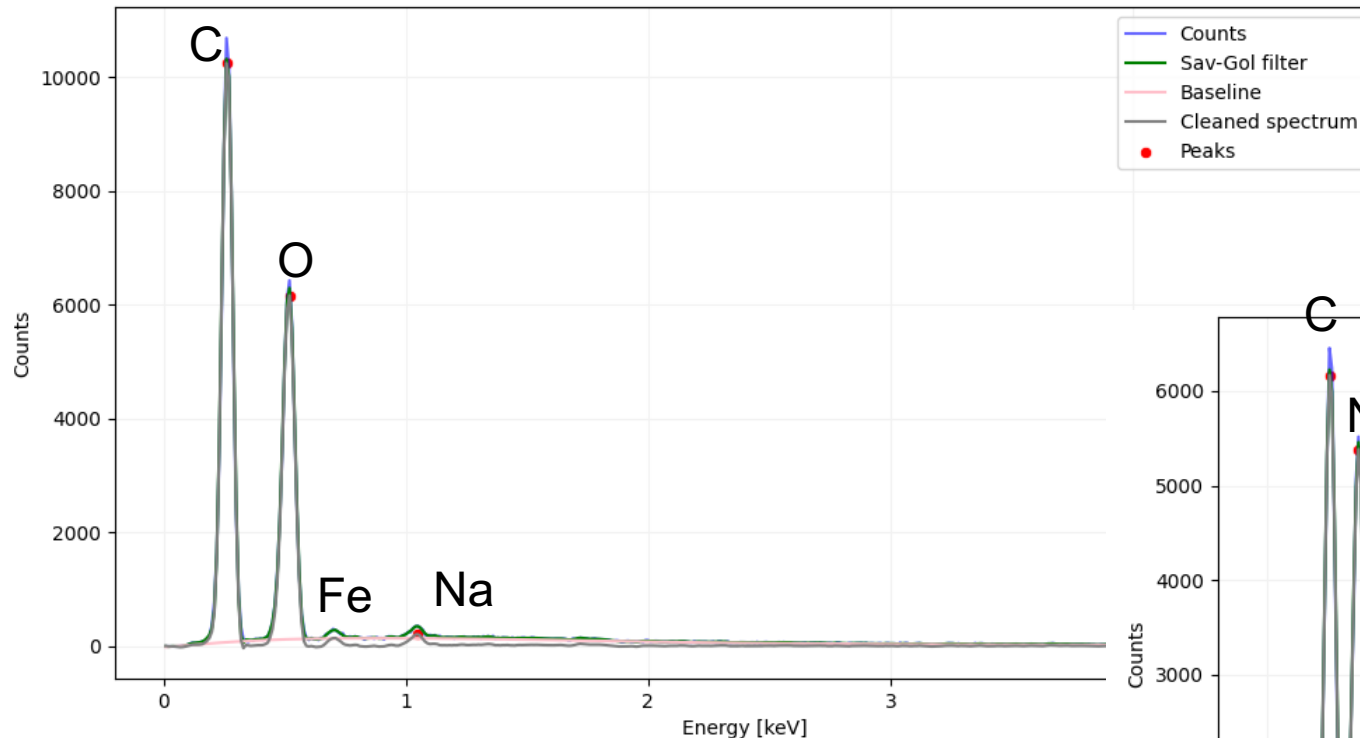
- Old Bakelite without linseed oil
- SE = surface irregularities, typical of non-oiled Bakelite
- BSE = clear material disuniformity
 - EDX to identify elements

- 2025 Bakelite without linseed oil
- SE = surface irregularities, typical of non-oiled Bakelite
- BSE = more material uniformity



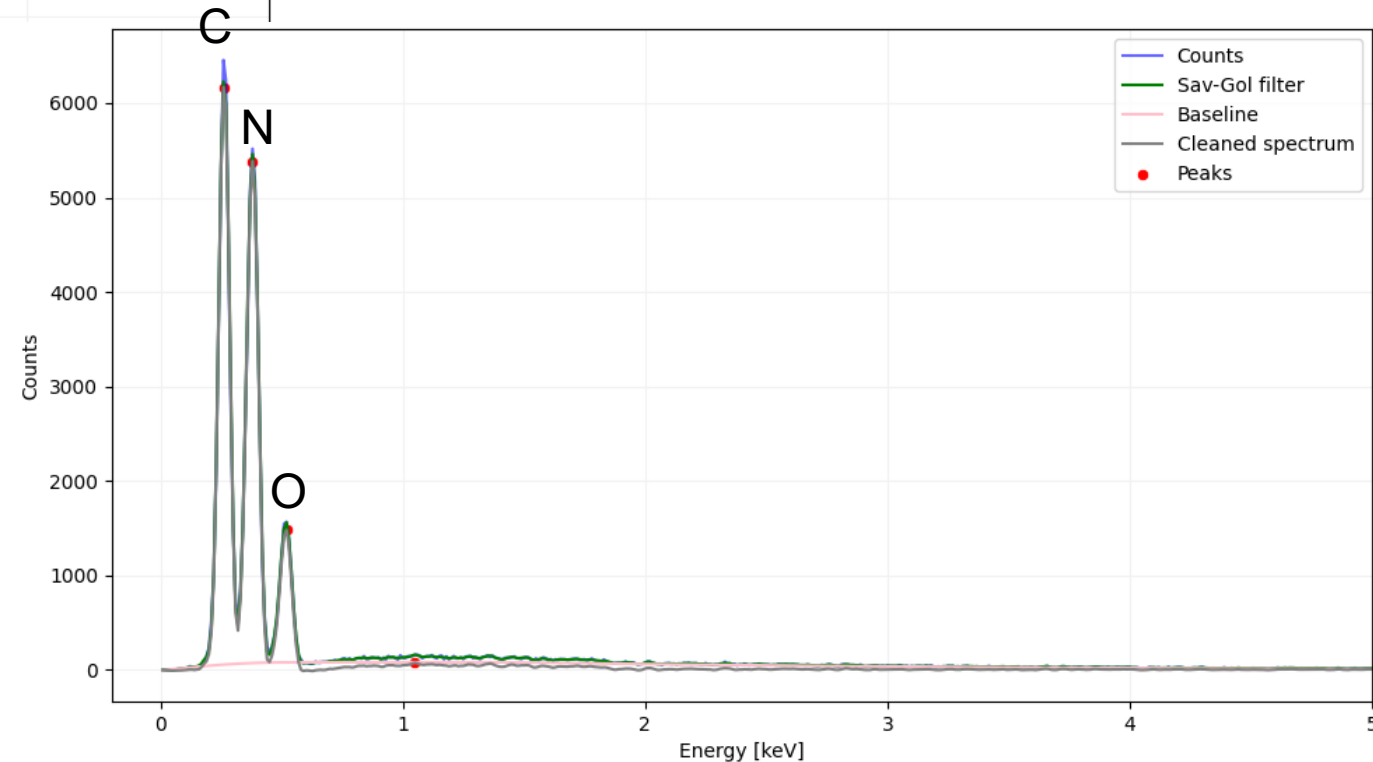
Bakelite
Top view

SEM results for virgin materials - 2



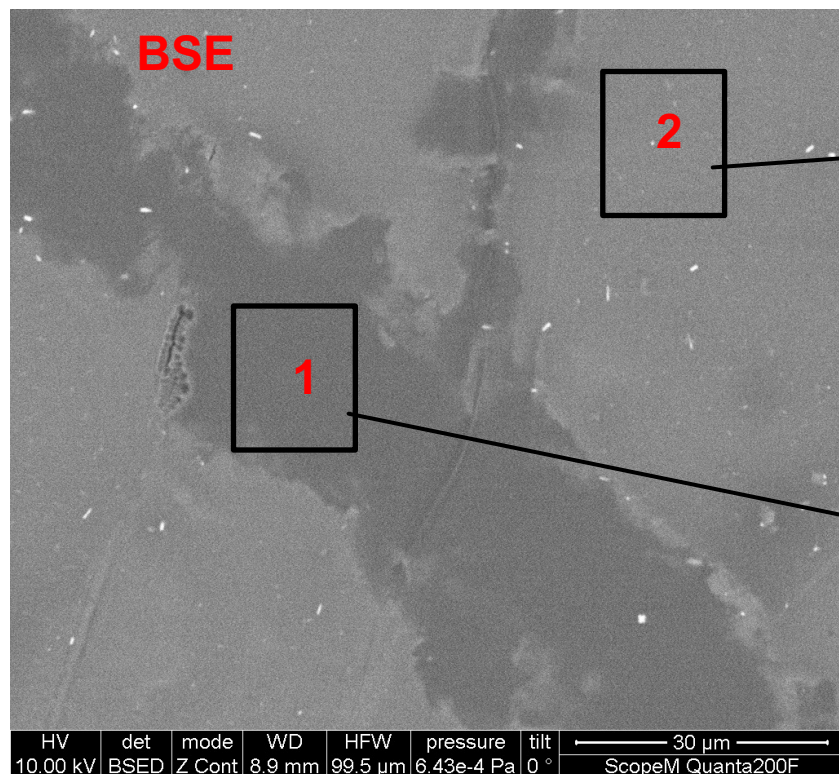
- 2025 Bakelite no oil
 - Presence on N
 - **Melaminic** resins used in production
 - No Fe + Na peak suppressed

- Old Bakelite no oil
 - No N
 - Phenolic resins used in production
 - **Fe peak = unknown origin**
 - Na peak = catalyst for reaction

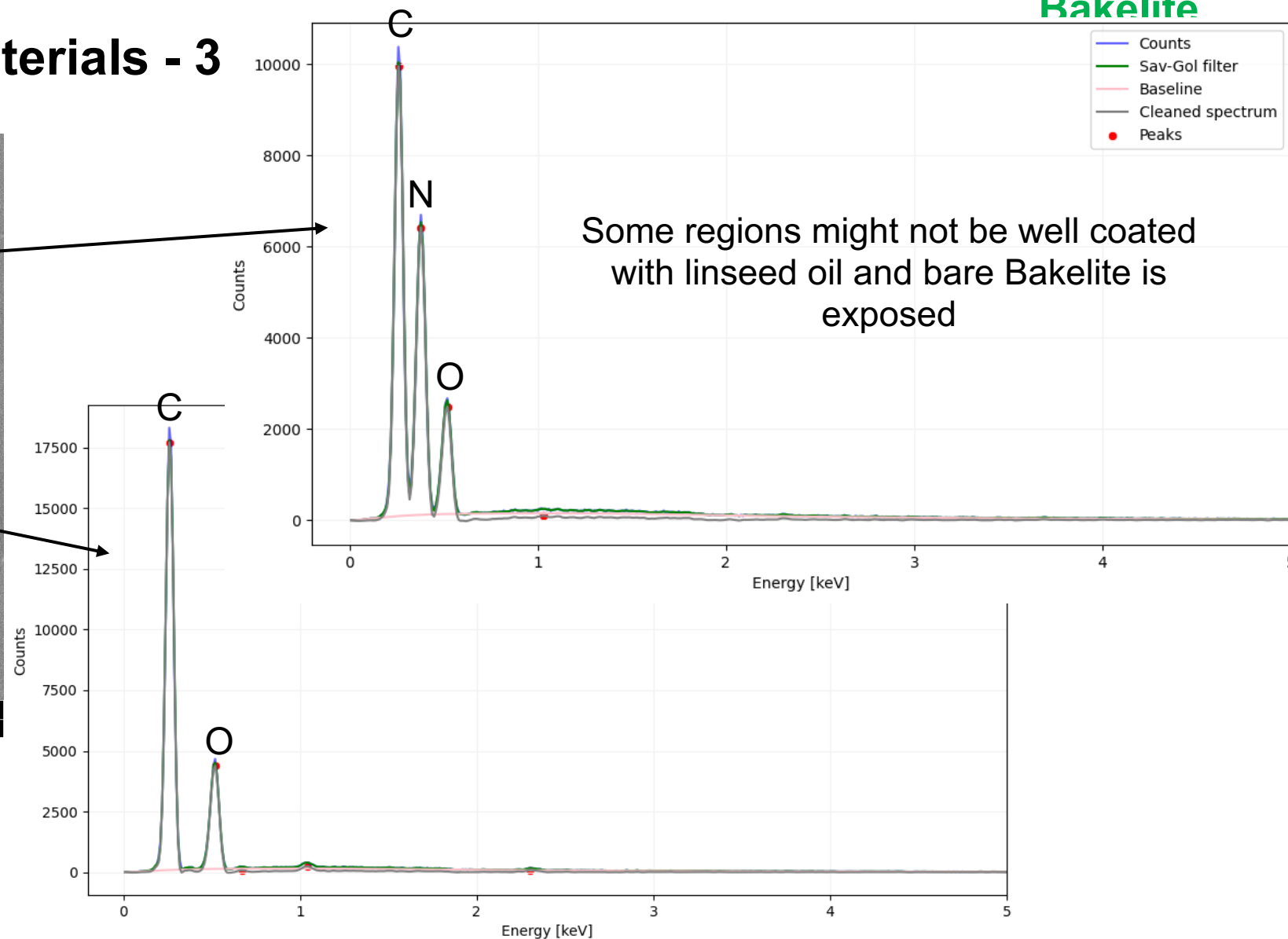


Bakelite

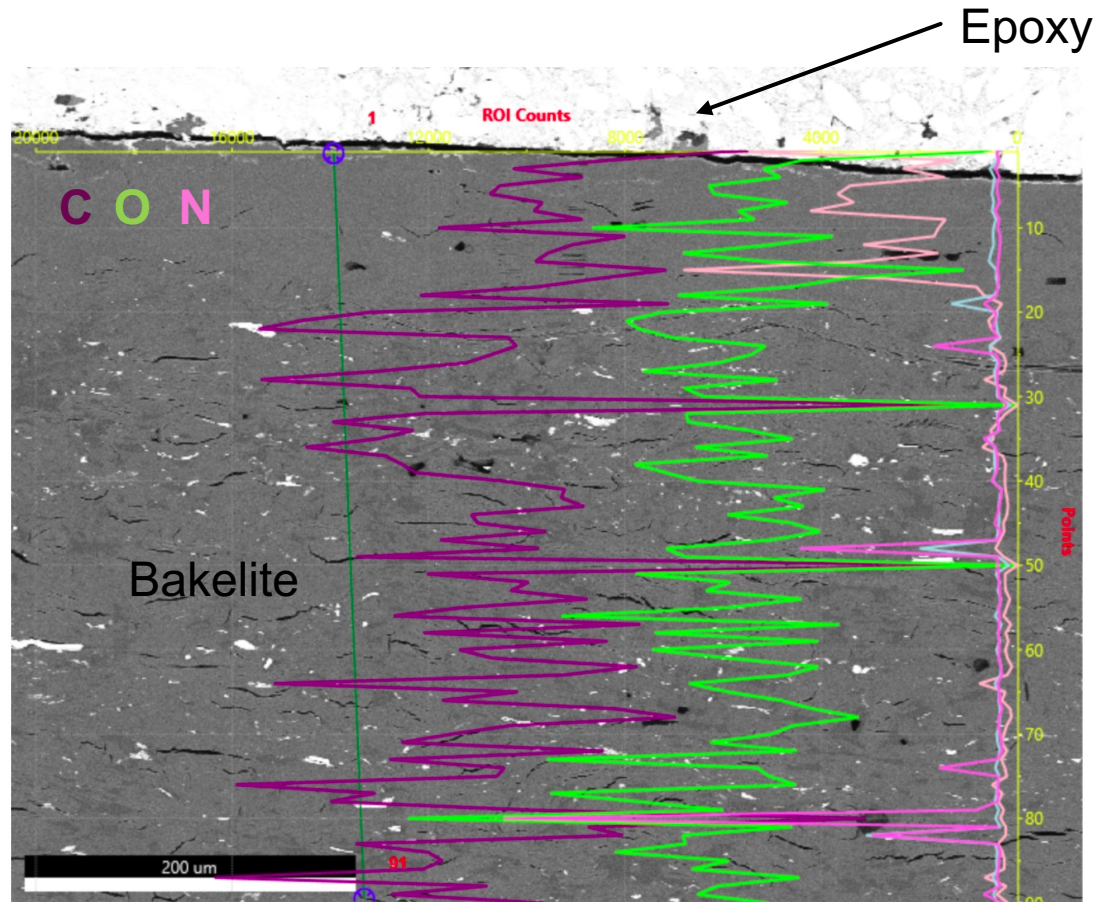
SEM results for virgin materials - 3



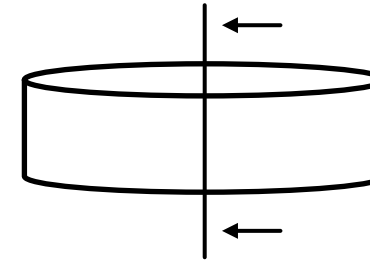
- Bakelite from unaged RPC
- BSE image non uniform



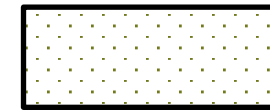
SEM results for virgin materials - 4



Bakelite Cross section view



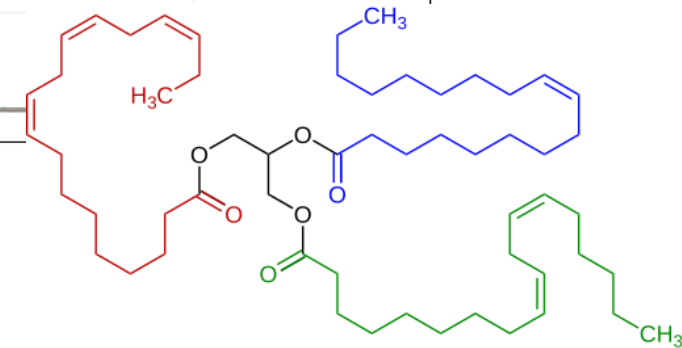
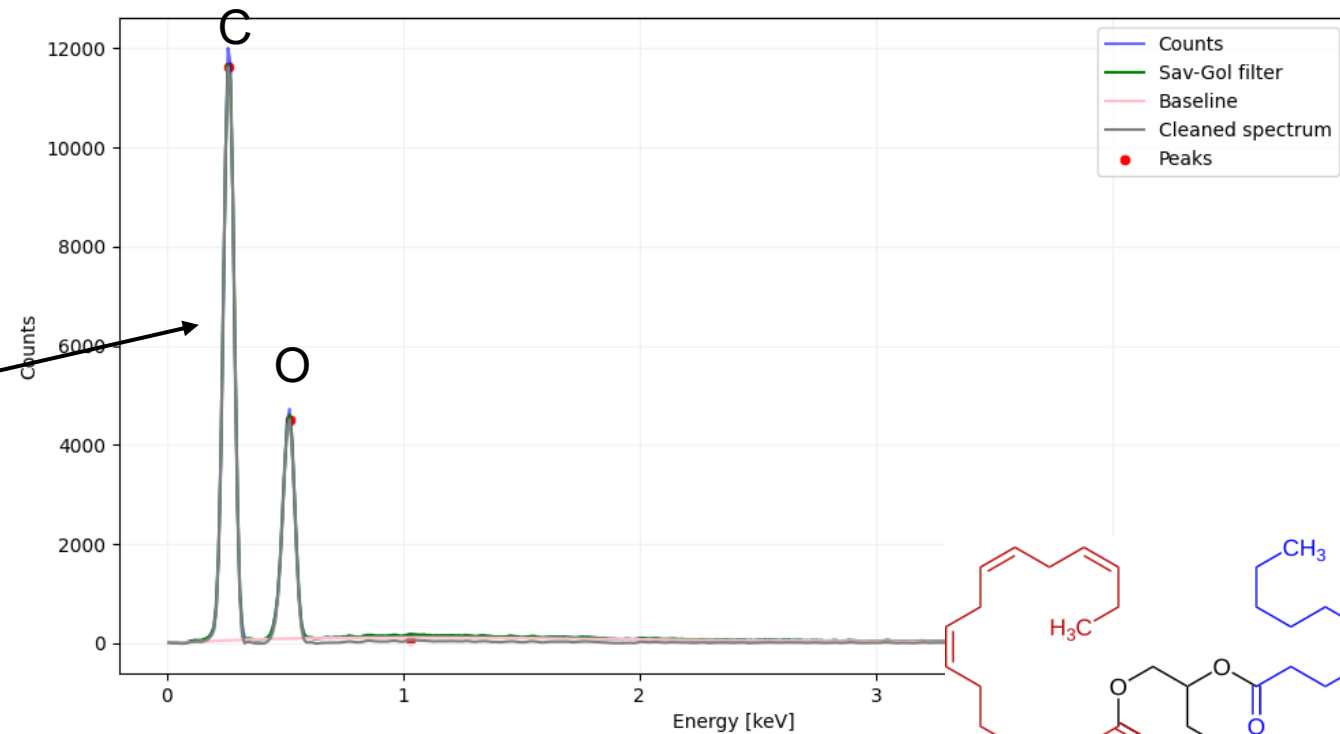
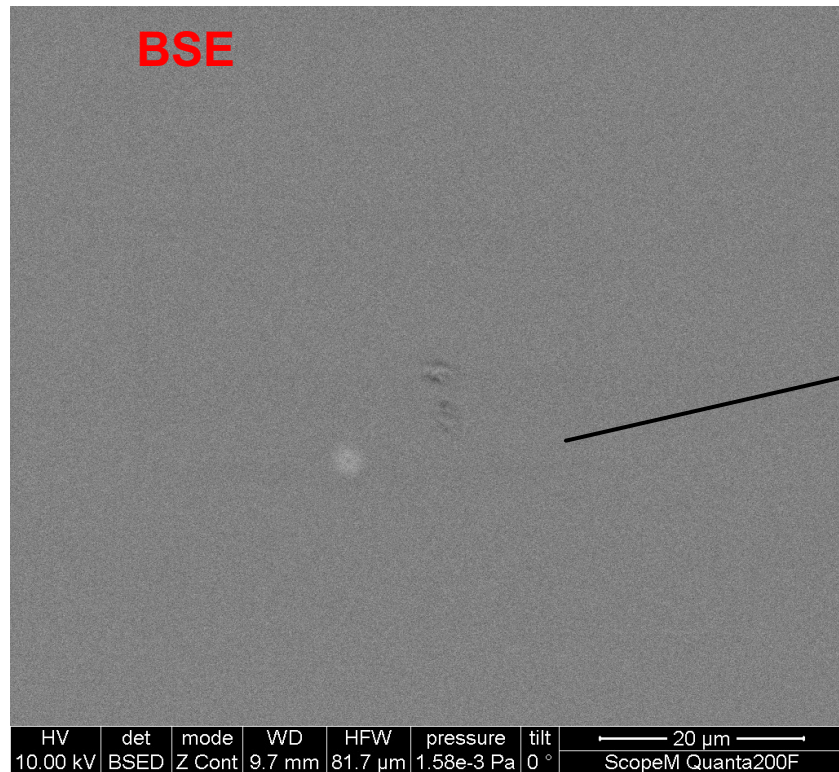
Cross section of the Bakelite sample



- Bakelite from 2021 unaged RPC, cross section view, embedded in Epoxy
- **EDX can be performed along a line**, point by point
 - Signal amplitude proportional to element concentration
- N concentration goes to zero at a few μm depth
 - **Melaminic** resin on top and phenolic more in depth

Bakelite
Top view

SEM results for virgin materials - 5

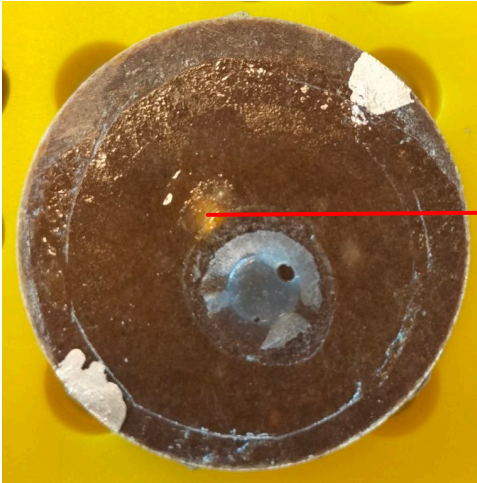


Representative triglyceride found in linseed oil

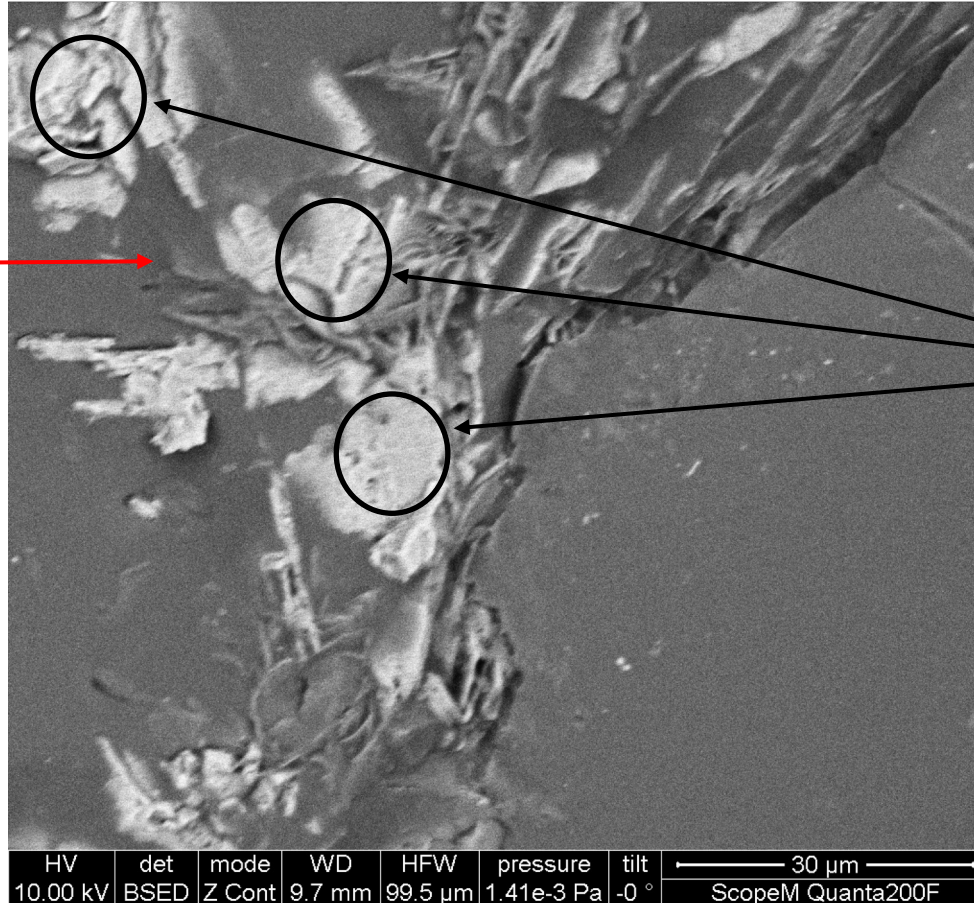
- Old Bakelite, oiled in house. Top view
- BSE image very uniform
 - Uniform elemental composition

Uniform linseed oil layer (**C** and **O** only)
-> Visual inspection of linseed oil layer possible

SEM analysis of defects on GIF++-aged RPC



Bakelite sample from HV electrode



SEM image of yellow dust

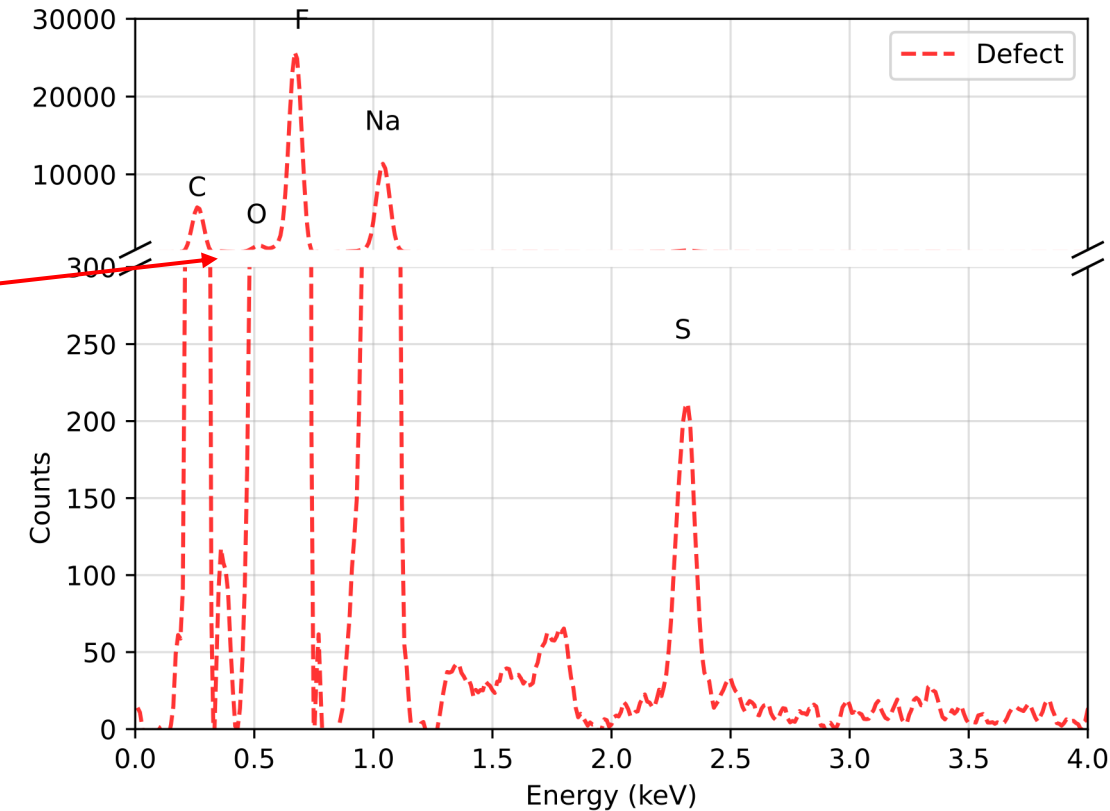
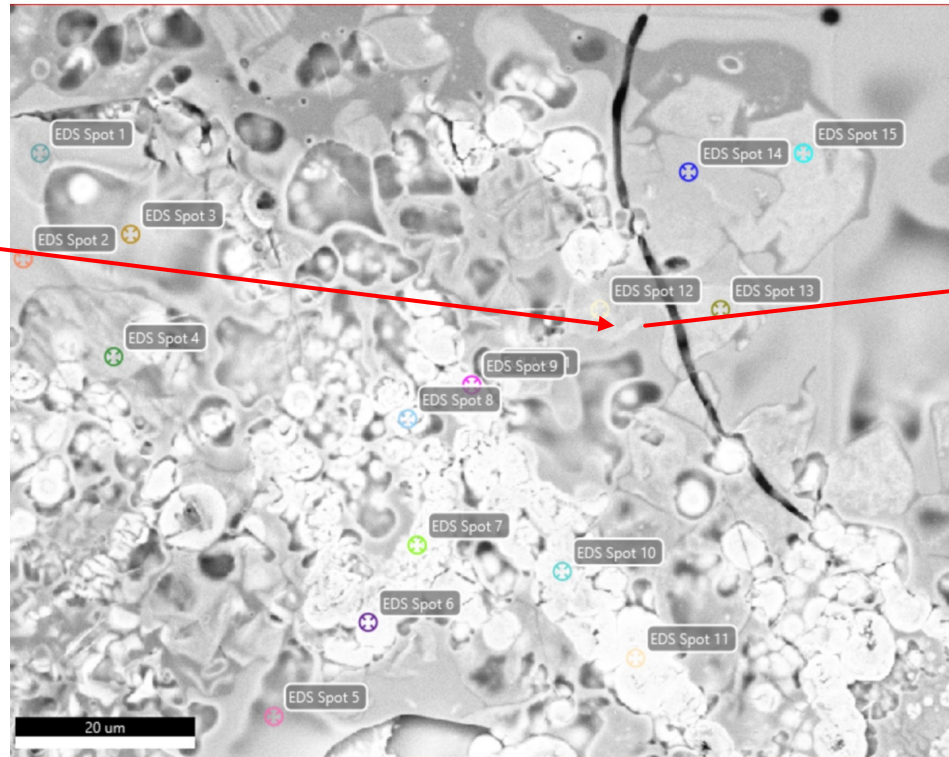
- BSE electrons
 - Information on material composition
 - Brighter areas = heavier elements
 - **Na richer areas**
 - Fluorine present everywhere

GND electrode

SEM analysis of defects on GIF++-aged RPC



Bakelite sample from GND electrode



EDX spectrum of white dust on the GND electrode

Marie Curie postdoctoral fellowship

- EU-funded fellowships with a focus on research + personal skills development
 - “Not a research grant but a grant for researchers”
 - Ment to be carried out by a single researcher
- Project must also include personal development and dissemination among the general public
- In my case: 2 years at ETH (with secondment at INP Greifswald) + 1 year in Torino, working on alternative gas mixture for Resistive Plate Chambers
- Personal development part of the project:
 - German class
 - Data management course
 - Lateral leadership workshop + leadership course
 - Time management class
 - Participation to EU researchers’ night + dissemination activities

Data/code organization

Compliance with EU regulations:
[FAIR](#) principles + [open science](#)

GitHub repository for all codes available at
this [link](#)

Zenodo repository for datasets available at
this [link](#)

↓
README files to describe folder organization
and codes within

↓
[Data management plan](#) explains the strategy
for data collection and the data organization

↓
Documentation in the making (e.g. methods
and similar) on CERN codimd and then
transferred to Zenodo

Timeline of the project

WP	Task (T)	1st year				2nd year				Return phase			
	Time (months)	M 0-3	M 3-6	M 6-9	M 9 -12	M 0-3	M 3-6	M 6-9	M 9 -12	M 0-3	M 3-6	M 6-9	M 9 -12
WP1 Management	T 1.1: Produce management documents												
	T 1.2: Progress meetings with supervisor												
WP2 Chemical analyses	T 2.1: analyses on new and HFO aged samples (GIF++)												
	T 2.2: analyses on new and HFO aged samples (mat comp)												
	T 2.3: analyses on new and HFO aged samples (plasma)												
WP3 Model development	T 3.1: comparison of new and HFO aged samples (GIF++)												
	T 3.2: comparison of new and HFO aged samples (mat comp)												
	T 3.3: comparison of new and HFO aged samples (plasma)												
	T 3.4: development of model to explain the observed effects												
WP4 Training and career development	T 4.1: German class + tandem												
	T 4.2: Lateral leadership class												
	T 4.3: Research Data Management												
	T 4.4: Time management												
	T 4.5: Leadership course in Torino												
WP5 Impact	T 5.1: Participate to International Conferences												
	T 5.2: Outreach activities												
	T 5.3: Communication activities												
Secondment													