



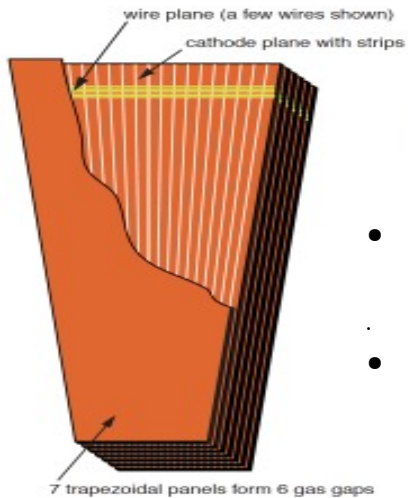
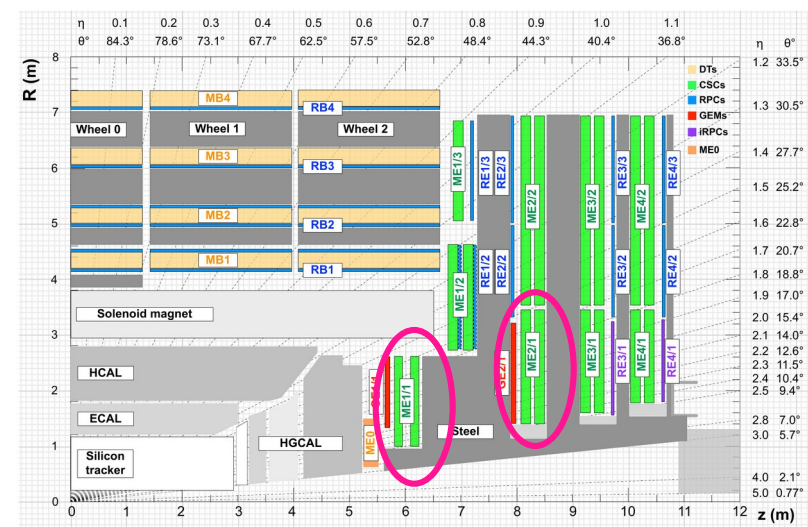
Studies toward reduction or replacement of CF_4 in the CMS CSC working gas mixture

K. Kuznetsova
for the CMS Muon group

3rd International Conference on Detector Stability and Aging Phenomena in Gaseous
Detectors

CMS CSC

- 6 layer MWPC with cathode planes machined into radial strips giving precise coordinate information across them
- **ME1/1** and **ME2/1** chambers – in the most forward location, differ in material and construction



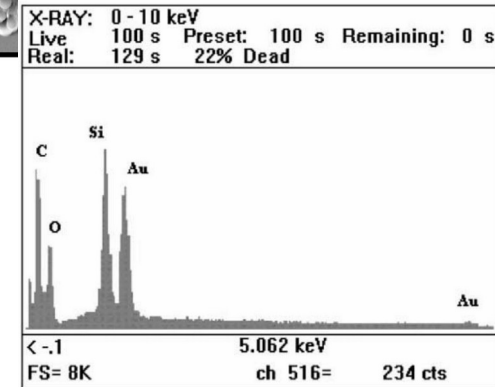
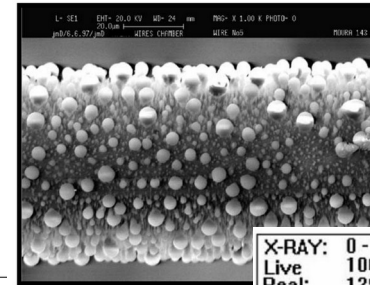
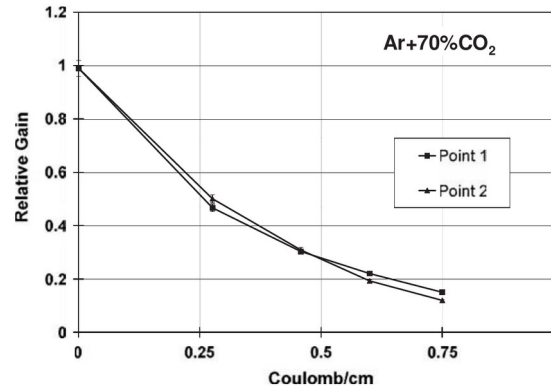
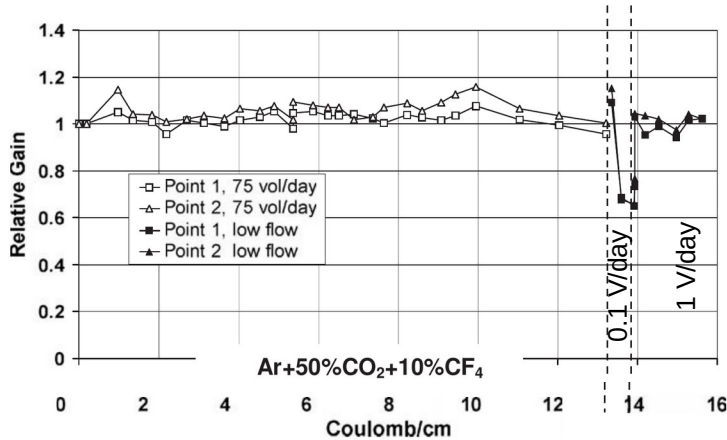
- **Cathode:** Cu-foil-coated glass-reinforced FR4 with strips milled into copper
- **Anode:** gold-plated tungsten wires, 50 μm in diameter (30 for ME1/1)

Prediction for High Luminosity LHC operation ($3000\ \text{fb}^{-1}$) for the most affected areas of ME1/1 and ME2/1 chambers:
 accumulated charge (longevity - related equivalent operation time) of **0.20** and **0.13 C per cm** of anode wire

CSC gas mixture

- 40% Ar + 50% CO₂ + 10% CF₄
- The main purpose of CF₄ in the gas mixture – protection against anode wire aging : $\text{Si} + 4 \text{F} \rightarrow \text{SiF}_4$ (also breaking C-chains in polymer formation)

Early studies with first CSC prototypes (Si in contact to the gas volume - not the case in the final design) NIM A 488 (2002) 240–257



CSC gas supply

- Developed and supported by CERN EP-DT
 - CSC: 540 chambers ~66 m³ in total
 - Total flow ~6.6 m³/h
 - 1 volume exchange per 6 (12) h for inner (outer) rings
 - Closed loop gas system
 - Replenishment rate: 10%
 - CF₄ recuperation : 50-70%
- **GWP(CF₄)~7000**
- **Increasing price**
- **Availability on market is getting unstable**

Three ways to reduce or eliminate CF₄ use or exhaust:

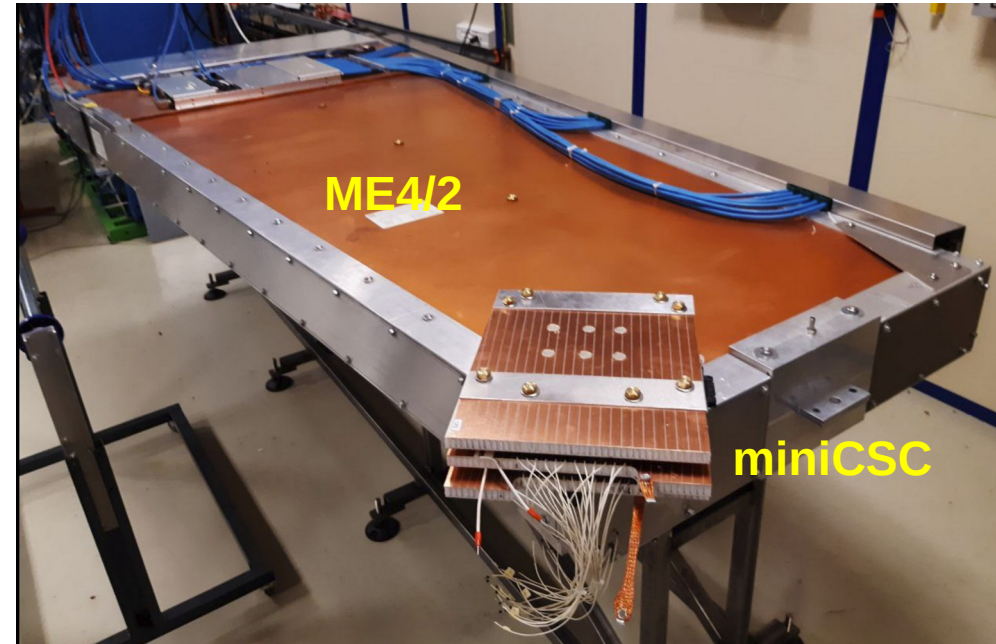
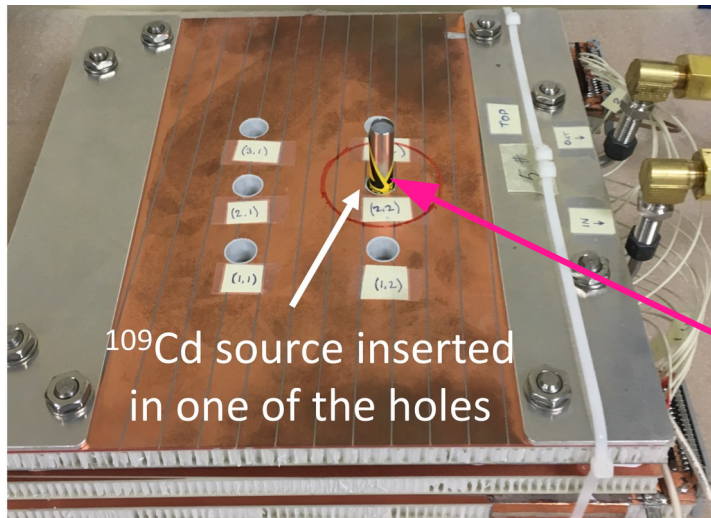
- **CF₄ recuperation:** EP-DT – efficiency of the CF₄ recuperation plant was increased from 30% to ~60% during Long LHC Shutdown 2019-2020
- **CF₄ reduction:**
 - lab studies with small prototypes ('miniCSC')
 - tests with full-scale production chamber at GIF++
- **Searches for CF₄ substitutes**

Any solution should preserve the CSC performance and longevity in view of HL-LHC

Reduction of CF4

Accelerated local irradiation of miniCSCs (ME2/1 type) with ^{90}Sr :

- Specially built prototypes
- 2 layers 30x30 cm²
- Original material
- Original technology
- Gas flow scaled to the chamber volume
- Open gas loop

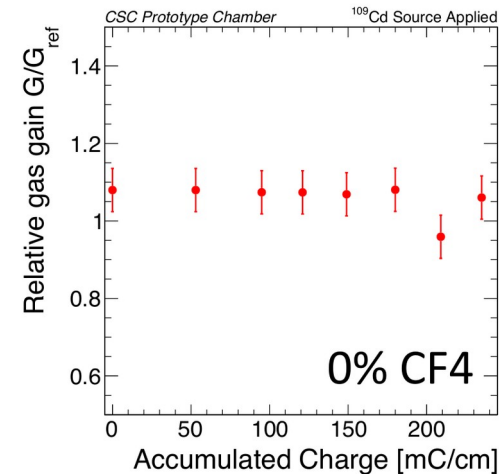
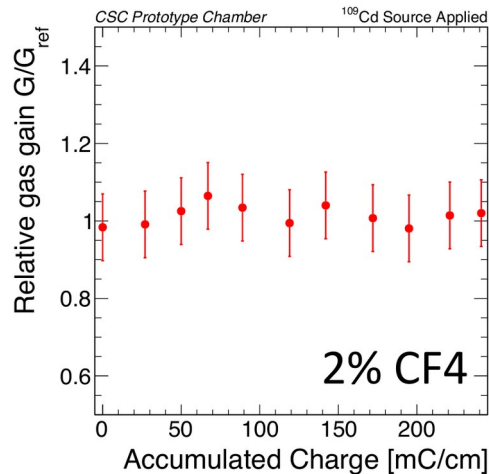
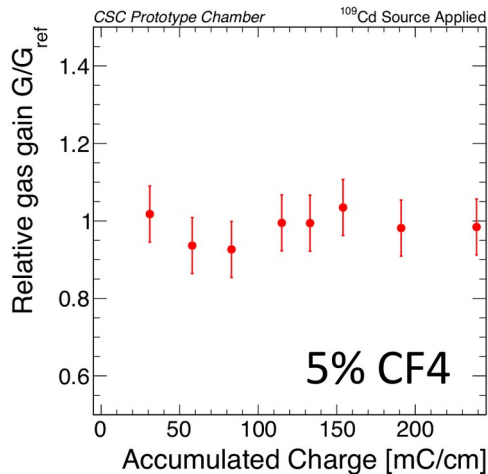


Irradiation (^{90}Sr) and control (^{109}Cd) points
Irradiation performed with acceleration factor ~ 100

Reduction of CF4

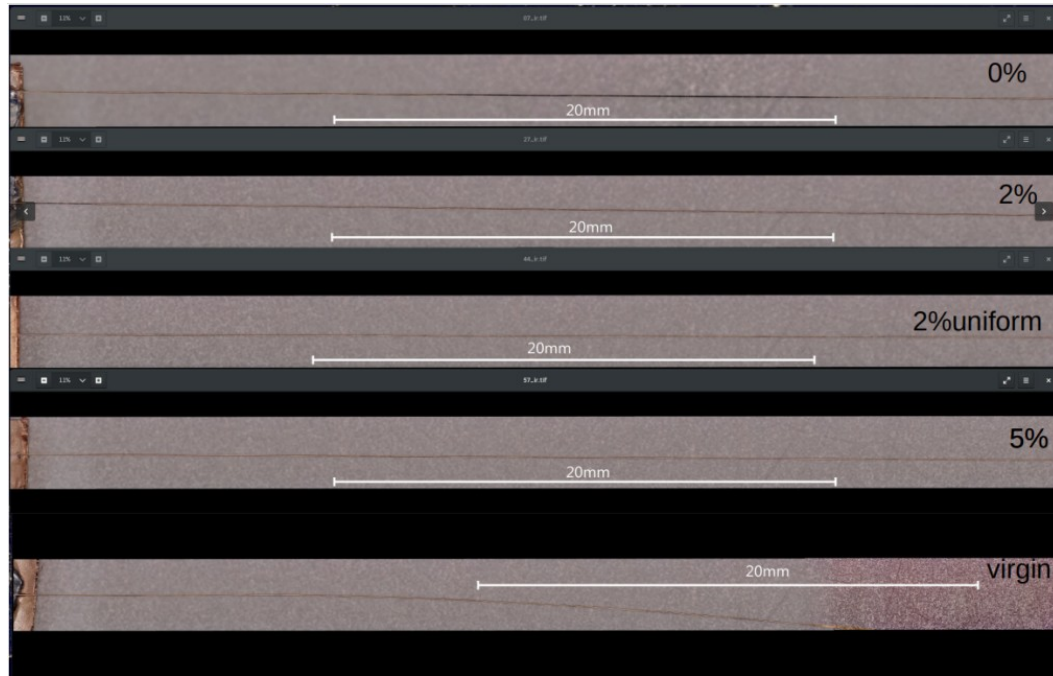
Accelerated local irradiation of miniCSCs (ME2/1 type) with ^{90}Sr :

- 5, 2 and 0% CF4 - performed at 904 and GIF++ up to 0.30 C/cm ($2.3 \times Q_{\text{HL-LHC}}$ for ME2/1)
- 10%CF4 was performed in PNPI up to 1.3 C/cm with high acceleration factor (~ 1000)
- **no significant performance degradation was seen in any of these longevity tests (gas gain, dark rate and current, interstrip resistance)**

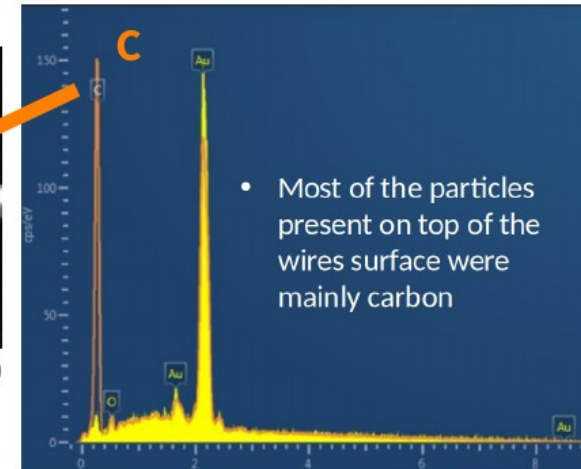
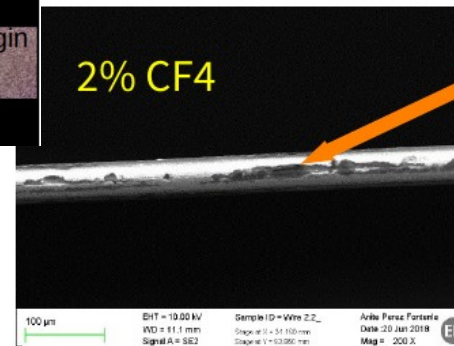


- cathode and anode surfaces were investigated after the tests (CERN, University of Belgrade, Sarov)
- cathode surface modification is seen in all cases
- **anode depositions are clearly seen for 2 and 0 %CF4 even with a naked eye**

Reduction of CF4 – anode surface

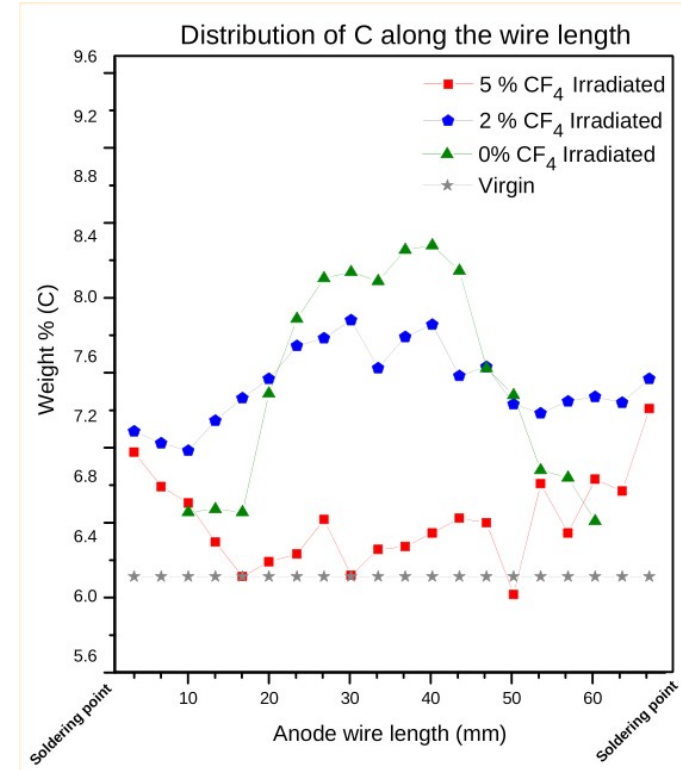
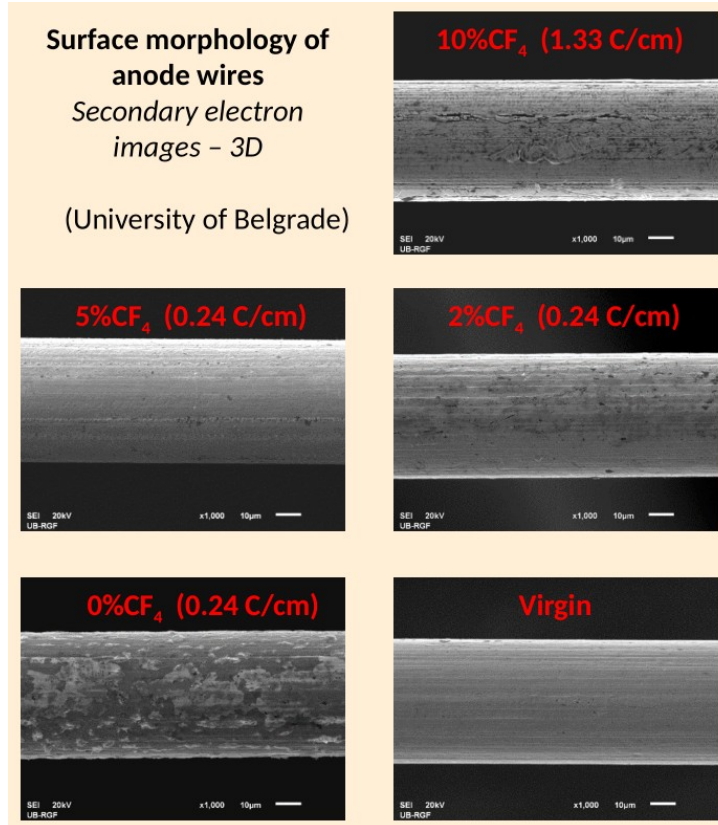


Optical microscopic view
and basic SEM/EDS
(CERN-MME-MM)



Reduction of CF₄ – anode surface

SEM/EDS
(University of
Belgrade) – talk
by Aleskandra
Radulovic on
Monday



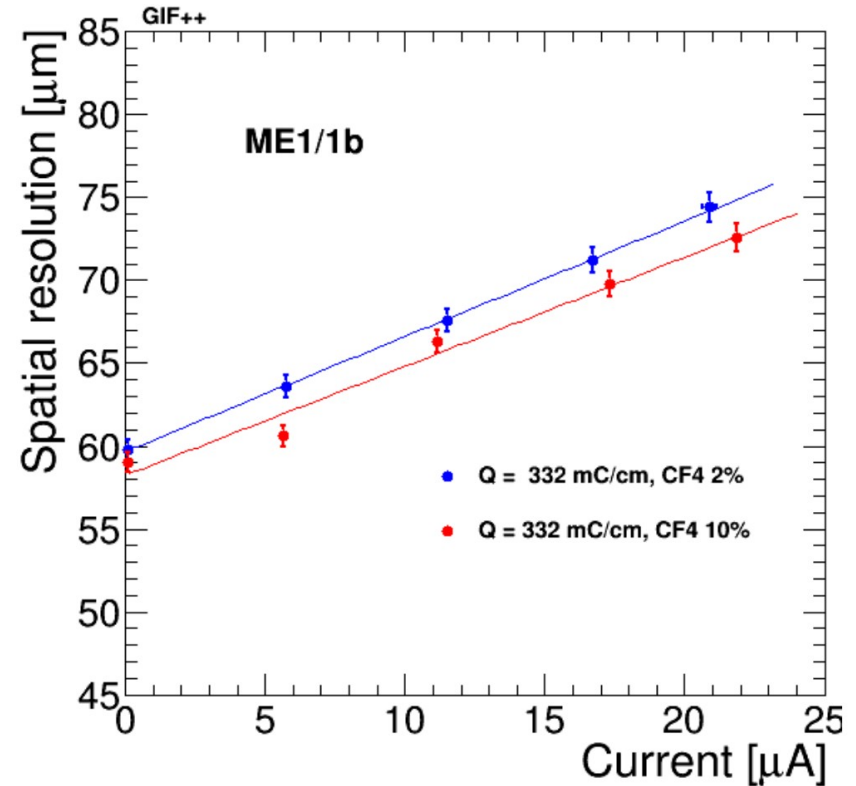
Though no miniCSC performance degradation has been seen in the longevity test – too low CF₄% seems to be risky! 5%CF₄ may be a good choice – also confirmed by the LHCb MUON operation experience => a longevity test with the full scale production CSCs are ongoing at GIF++ with 5%CF₄

CSC performance with the reduced CF4 content

Comparison of the CSC performance for muon detection has been done with ME1/1 and ME2/1 chambers during a muon test beam at GIF++

The measurements are done with different background levels up to the one comparable to HL-LHC (see talk of Victor Perehlygin)

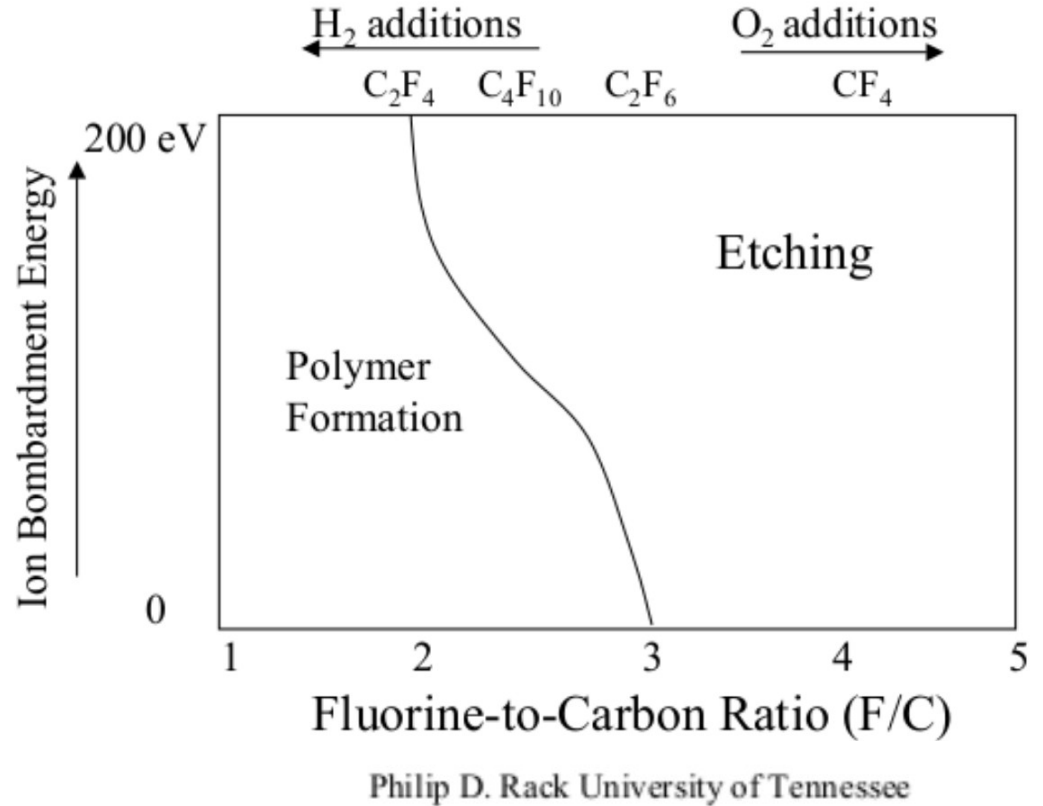
No significant difference between 2% and 10% CF4 gas mixtures was observed



Searches for CF₄ replacement

Reasonable low GWP candidates:

- Compounds (gases) containing F with
 - relatively short molecular chain (<5)
 - low GWP (<500)
- These candidates should be
 - not hazardous (toxic, flammable, etc.)
 - have reasonable boiling point
- **F/C ratio plays significant role for Si etching**
=> relatively high F/C ratio



Searches for CF4 replacement

- Most (hydro)fluorocarbons with relatively short chains and relatively low GWP (<500) are toxic or flammable...

(exception) – CF3I – tried – too electronegative

- Molecules with long chain may tend to polymerize, i.e. may cause anode/cathode ageing

- **GWP(CF4) = 7390**
- all perfluorated gas compounds except CF3I have larger GWP
- only HFC/HCFC/HFE with GWP < 500 are listed
- Fluorinated alcohols not included due to -OH group
- **Flammability** (may be different in different systems):
 - **F**=flammable, **HiF**=highly flammable, **ExtF**=extremely flammable

			GWP	F:C ratio	remarks
	Carbonyl fluoride	COF2	1	2:1+O	extremely toxic
	Trifluoriodomethane	CF3I	0.4	3:1	tried, electronegative
Halon-1202	CAS: 75-61-6	CBr2F2	231	2:1	Irritant; bp=26°C;
Halon-2311	CAS: 151-67-7	C2HBrClF3	41	3:2+Cl	Irritant, toxic. bp=53°C;
HFC-41	Fluoromethane	CH3F	92	1:1	F
HFC-143	1,1,2-Trifluoroethane	CHF2-CH2F	353?	3:2	ExtF
HFC-152	1,2-Difluoroethane	CH2F-CH2F	53	2:2	toxic; bp=31°C
HFC-152a	1,1-Difluoroethane	CHF2-CH3	124	2:2	ExtF; toxic??
HFC-161	Fluoroethane	CH2F-CH3	12	1:2	ExtF
HFC-263fb	1,1,1-Trifluoropropane	CH3-CH2-CF3	76	3:3	F
HFC-272ca	2,2-Difluoropropane	CH3-CF2-CH3	144	2:3	

HFC (single bonds)

Increasing chain length

HFO (a double bond)

			GWP	F:C ratio	remarks
HFC-1132a	Vinylidene fluoride	CH ₂ =CF ₂	<1	2:2	ExtF, toxic
HFC-1141	Vinyl fluoride	CH ₂ =CHF	<1	1:2	ExtF
HFC-1225ye	1,2,3,3,3-Pentafluoropropene	CF ₃ CF=CHF	<1	5:3	Irritant
HFC-1234yf	2,3,3,3-Tetrafluoroprop-1-ene	CH ₂ =CF-CF ₃	4	4:3	F
HFC-1234ze(E)	trans-1,3,3,3-Tetrafluoroprop-1-ene	CHF=CH-CF ₃ (E)	7	4:3	
HFC-1243zf	3,3,3-Trifluoropropene	CF ₃ CH=CH ₂	<1	3:3	F, toxic
HFC-1336mzz(Z)	cis-1,1,1,4,4,4-Hexafluorobut-2-ene (CAS:692-49-9)	CF ₃ -CH=CH-CF ₃ (Z)	9	6:4	no hazards, pb=33°C;
HFC-1336mzz(E)	trans-1,1,1,4,4,4-Hexafluorobut-2-ene (CAS:66711-86-2)	CF ₃ -CH=CH-CF ₃ (E)	18	6:4	no hazards, pb=8°C;
HFC-1345zfc	3,3,4,4,4-Pentafluorobut-1-ene	C ₂ F ₅ -CH=CH ₂	<1	5:4	F

Increasing chain length

HCFC

HCFC-1224yd(Z)	cis-1-Chloro-2,3,3,3-tetrafluoroprop-1-ene	CHCl=CF-CF ₃ (Z)	1	4:3+Cl	no hazard info; Ashai Glass (Japan)
HCFC-1233xf	2-Chloro-3,3,3-trifluoroprop-1-ene	CH ₂ =CCl-CF ₃	1	1:3+Cl	F, irritant
HCFC-1233zd (E)	trans-1-Chloro-3,3,3-trifluoroprop-1-ene	CHCl=CH-CF ₃ (E)	4.5	3:3+Cl	no hasards; ATL-RPC
HCFE-235da2	Isoflurane	CHF ₂ -O-CHCl-CF ₃	350	5:3+Cl+O	toxic

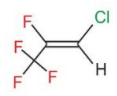
HFE

HFE-143m		CF ₃ -O-CH ₃	750	3:2+O	JINST13 P03012; bp=-24°C
HFE-236fa	CAS: 20193-67-3	CF ₃ -CH ₂ -O-CF ₃	487	6:3+O	bp=62°C
HFE-245fa1	CAS: 84011-15-4	CHF ₂ -CH ₂ -O-CF ₃	286	5:3+O	bp=26°C
HFE-245mc		CF ₃ -CF ₂ -O-CH ₃	622	5:3+O	JINST13 P03012 ; bp=5°C
HFE-254cb2	CAS: 425-88-7	CH ₃ -O-CF ₂ -CHF ₂	359	4:3+O	HiF; irritant
HFE-263fb2	CAS: 460-43-5	CF ₃ -CH ₂ -O-CH ₃	11	3:3+O	no hazard info; bp=31°C;
HFE-338mmz1	CAS: 26103-08-2	(CF ₃) ₂ CH-O-CHF ₂	380	8:4+O	bp=40°C;

Increasing chain length

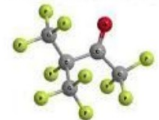
Other possibilities?

SF6 alternatives research still ongoing in electrical industry




HCFO-1224yd


Amolea
GWP < 1
X



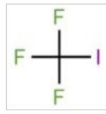
Novoc 5110
GWP < 1
X



Novoc 4710
GWP 2100
X



C₄F₈O
GWP 8700
X



CF₃I
GWP < 1
X

CF₃C(O)CF(CF₃)₂ iso-C₃F₇CN

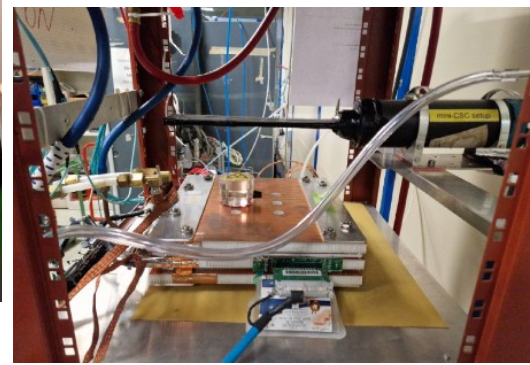
? ? Gianluca Rigoletti

Searches for CF4 replacement

- Not so many choices...
- The two ethers from the JINST publication have GWP slightly above the cut (500) but still ~10 times better than CF4
- Molecules with long chain may tend to polymerize, i.e. may cause anode/cathode ageing
- **HFO-1234ze** – does contain F, but **F:C** ratio is not optimal (**4:3**)
- **HFO-1336mzz(E)** – preliminary looks reasonable – better **F:C** ratio (**6:4**) ==> **availability??!**
 - ...and longer molecular chain
- Hydrochlorofluorocarbons (HCFC) – HCFC-1233zd(E) – poor **F:C** ratio (**3:3**) and **chlorine** containing ==> of low interests for CSC
- Hydrofluoroethers (HFE, R-O-R') – **HFE-245fa1 (5:3)** and **HFE-143m (3:2)**
 - contain oxygen
 - listed in **JINST13 P03012** as being of potential interest for gas detectors ==> **availability??!**
- Novec gases to be investigated

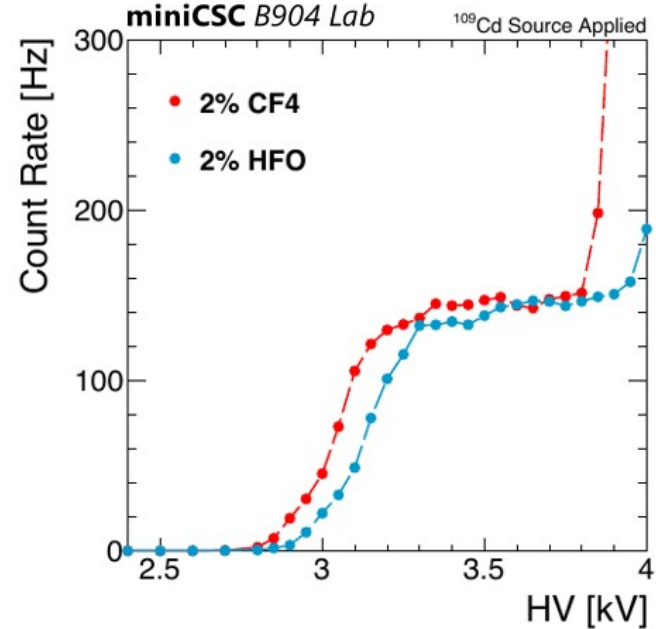
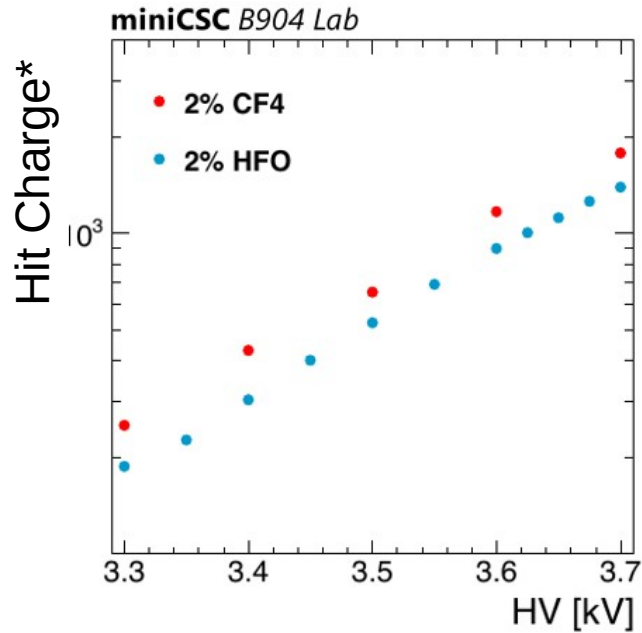
Searches for CF4 replacement

- HFO1234ze preliminary studies – see next slides
- Limited availability and high price for other candidates – still searching for them
- Easier solutions? Adding O2 to very small admixtures of CF4? To be studied...
- (Semi-)liquid ethers?
- Finalizing development in CMS b904 CSC lab at CERN
 - miniCSC production – 6 new prototypes
 - irradiation and measurement setup
 - dynamic mixing gas system based on the EP-DT design – 4 input channels
 - fast mixture property studies with a straw tube



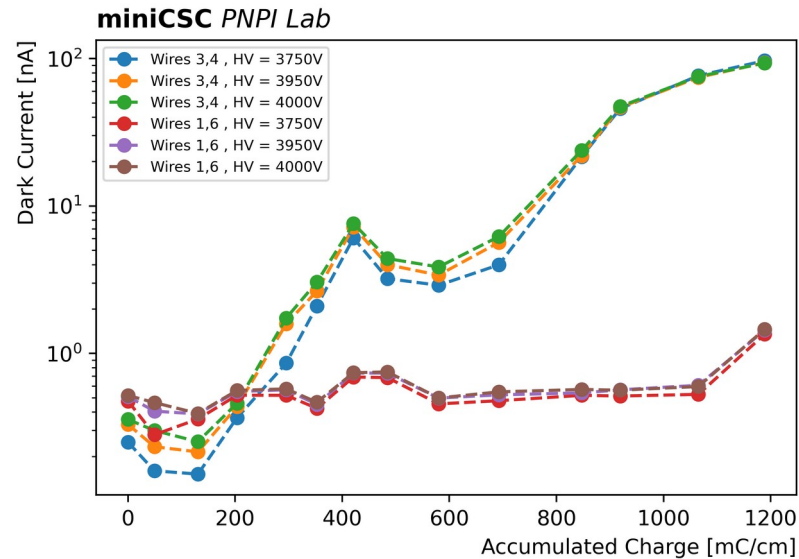
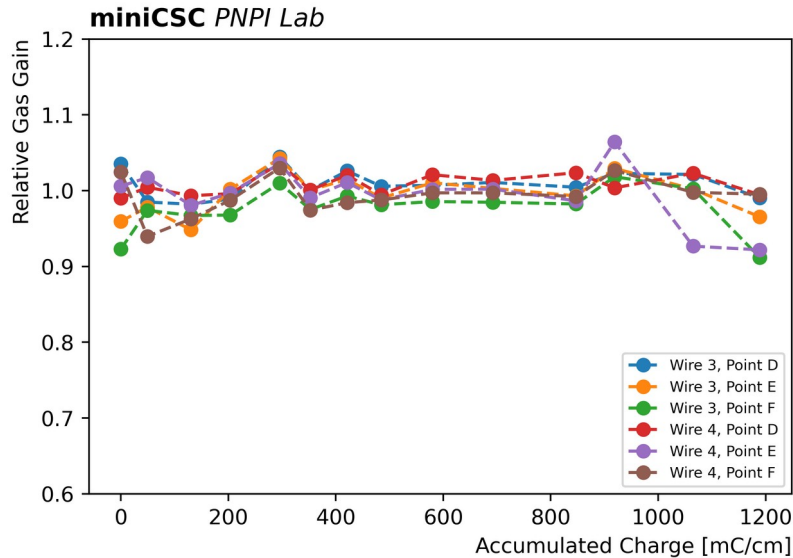
HFO1234ze

- Quick performance test with miniCSC comparing 2%CF4 and 2%HFO1234ze mixtures
- Just 100V increase in working voltage, good efficiency, reasonable plateau length



HF01234ze

- First very accelerated longevity test – local ^{90}Sr irradiation, open loop, no O₂/H₂O monitoring
- No gas gain reduction up to 1C/cm but **significant increase in dark current** during irradiation

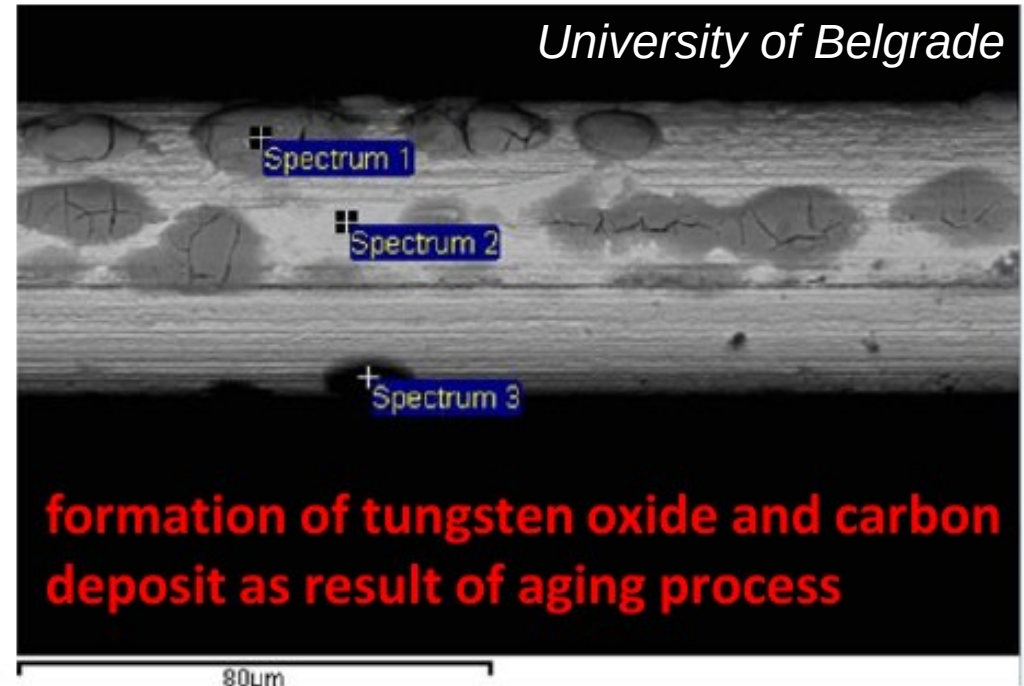


Assuming the extra-currents coming from the irradiation spot: **10 nA from ~2 cm** of irradiated wire scaled to 200 m of ME2/1s1 wires give 100 uA...

Test to be repeated in more controlled conditions

HF01234ze

- EDS/SEM analysis: in contrast to Ar/CO₂ and Ar/CO₂/CF₄ gas mixtures we see significant modification of the anode wire surface with tungsten oxide on the wire surface



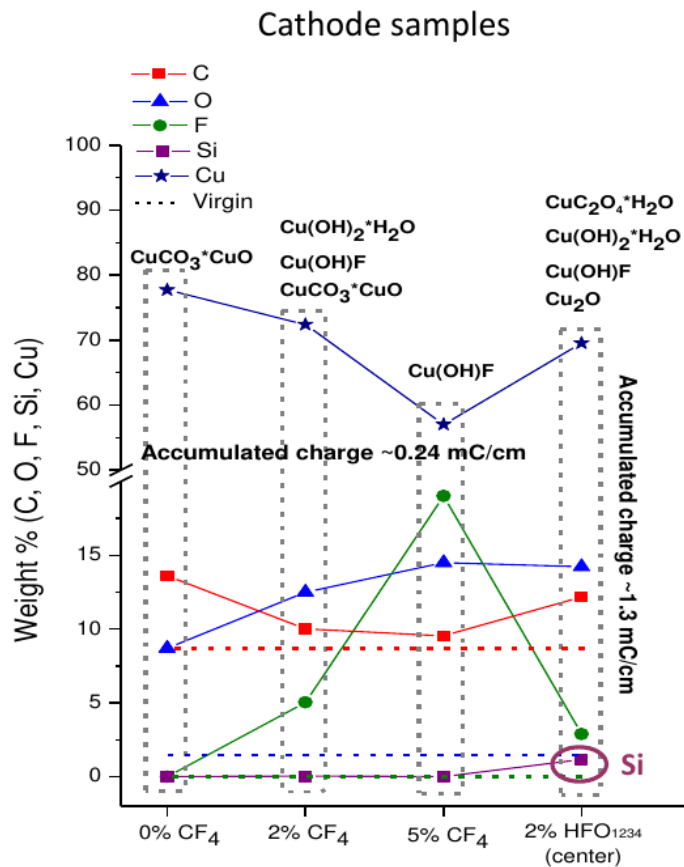
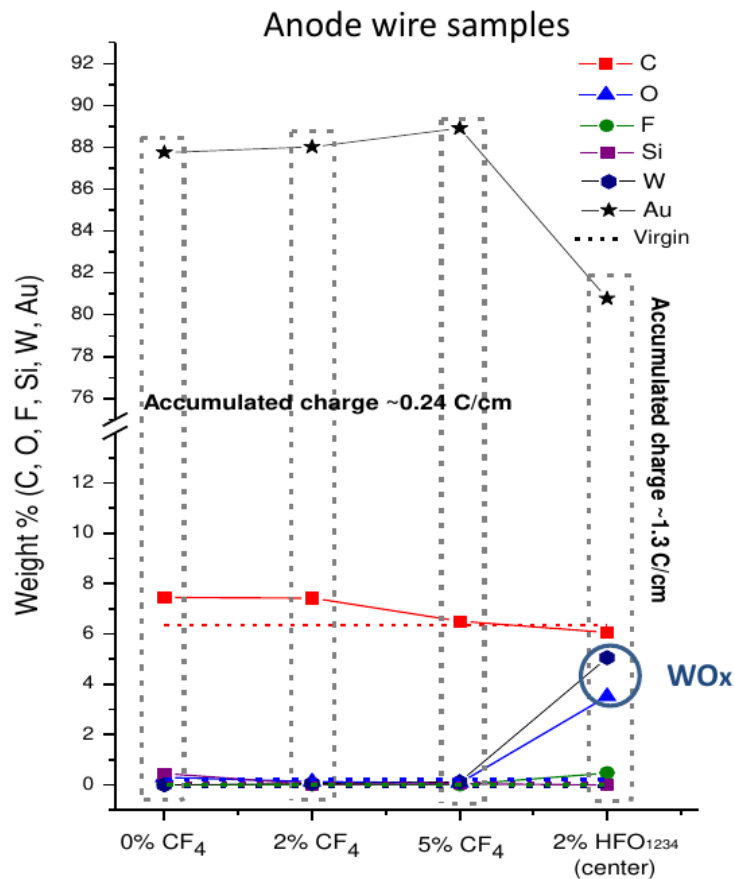
All results in weight%

Spectrum	In stats.	C	N	O	F	Al	Si	Cl	W	Au	Total
Spectrum 1	Yes	4.86	0.00	24.42				0.00	69.83	0.88	100.00
Spectrum 2	Yes	5.61	4.75	1.13				0.00	4.57	83.95	100.00
Spectrum 3	Yes	60.95	5.87	3.85	5.86	0.71	0.21	0.69	0.37	21.47	100.00

Irradiated electrode analysis

University of Belgrade

Lessons learned:



- Hydroxyl and hydrate groups seen in the XRD results indicate possible presence of H₂O - monitoring of H₂O and O₂ is needed during the irradiation tests
- Comparative material analysis approach is developed together with Belgrade colleagues - is a powerful tool in understanding plasma chemistry processes in MWPC
- HFO1234ze test to be repeated with lower acceleration factor up to comparable charges

Summary and next steps

- **Searches for new mixtures is a complex and ambitious task** involving
 - Understanding of plasma chemistry processes in the detector volume – can be probed with
 - Simulation of the chemical reaction (requires common work with chemists)
 - Measurements during irradiation? (talk by Maria Cristina Arena)
 - Laboratory performance and irradiation tests – well developed
 - Material analysis of the irradiated electrodes – developed during analysis following the first irradiation tests (talk by Aleksandra Radulovic)
- **CMS b904 CSC lab at CERN – finalizing the setup development :**
dynamic gas mixing system + set of miniCSC + irradiation/measurement setup
=> many thanks to CERN EP-DT gas group (gas system) and to CMS mechanical workshop (miniCSC)
 - Local irradiation with more controlled conditions (O₂/H₂O monitoring)
 - Scheduled performance and longevity tests with HFO1234ze, recuperated CF₄, CF₄+O₂
- **Searching for alternative gases of interest on the market** (together with EP-DT gas group)
- **Work on irradiated material analysis** together with Belgrade
- **Deeper involvement of chemists expertise** on the prediction of gas properties

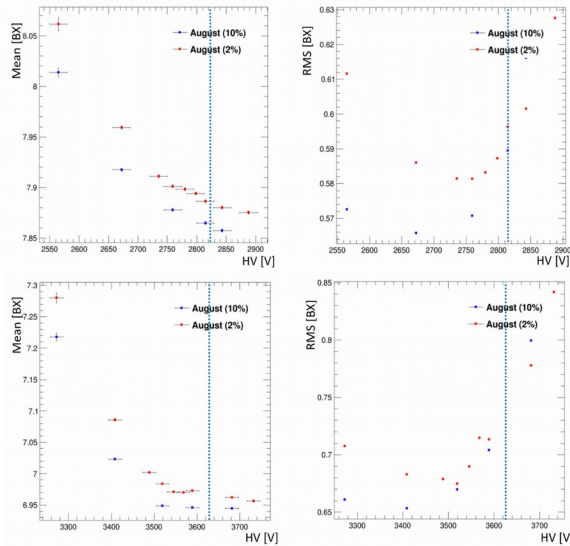
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Update on comparison of 10% and 2% CF4 mix

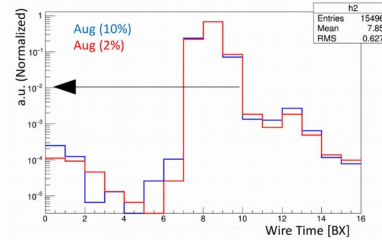
Wire hit time distribution: 40%Ar+50%CO2+10%CF4 vs 40%Ar+58%CO2+2%CF4

work in progress
B.Joshi (UF)

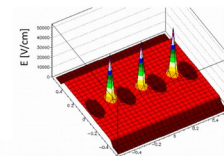
Mean and RMS of the distribution



No noticeable difference in signal timing for 2% and 10% CF4 mixtures



In agreement with expectations from Magboltz calculations:



S. Nasybulin (PNPI)

