Searches for CF4 replacement for the CSC gas mixture

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Mini-Workshop on gas transport parameters for present and future generation of experiments
22/04/21

CF4 in the CSC gas mixture

- **CMS CSC nominal gas mixture: 40% Ar + 50% CO_2 + 10% CF_4**
  - **CF_4** : **protection against anode ageing**
  - *In such a small quantity CF_4 does not change significantly the properties of the Ar/CO_2 mixture => the presence of CF_4 provides longevity only*

- **CF_4 - a source of fluorine radicals**

  + protects against Si-based depositions : Si/SiO_2+4F→ SiF_4 (+O_2)

  + protects against polymer film formation (in presence of oxygen radicals)

  - in a large quantity may cause wire "corrosion"

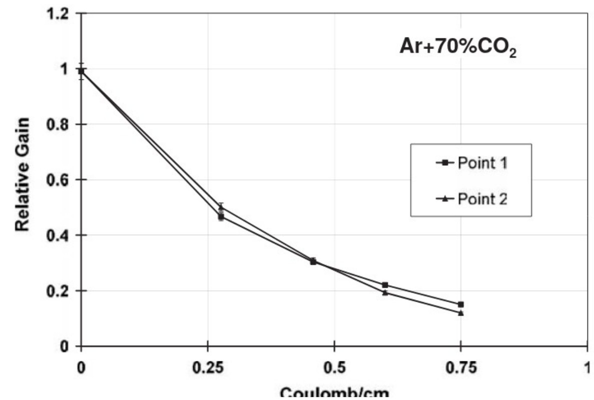
- Practical experience of CF_4 usage in MWPC gas mixtures is well systematized

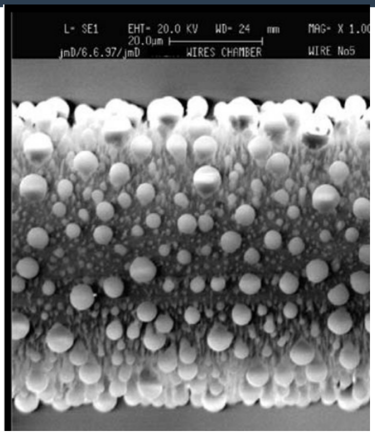
  (for example, overview by Mar Capeans here)

- CF_4 is widely used in plasma etching of Si/SiO_2 wafers and polymer films – more theoretical knowledge and even simulations are available, however for the specific conditions (pressure, energies, flows etc)

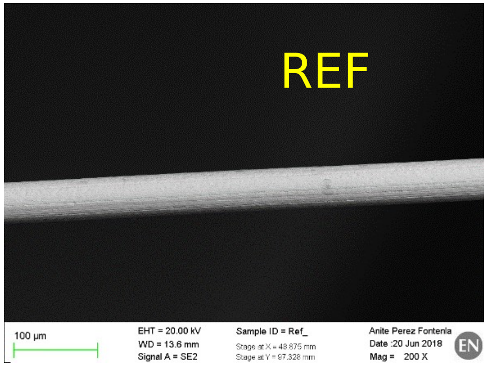
CF4 - do we need it in CSC?

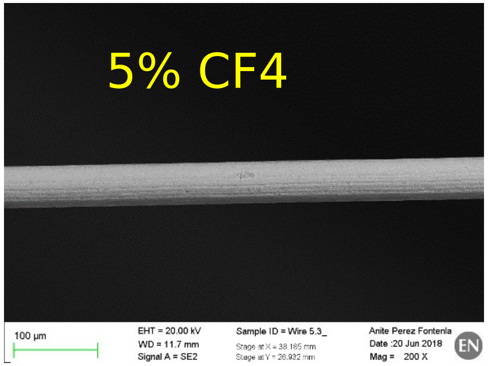
- Pre-construction studies with CMS CSC prototypes of **early design** (Si-containing material in contact with gas volume, not present in the final CSC design) – **rapid gain drop under irradiation for Ar/CO2** mixture and no significant degradation and **no anode wire deposition** up to at least 12 C/cm for Ar/CO2/**10%CF4**

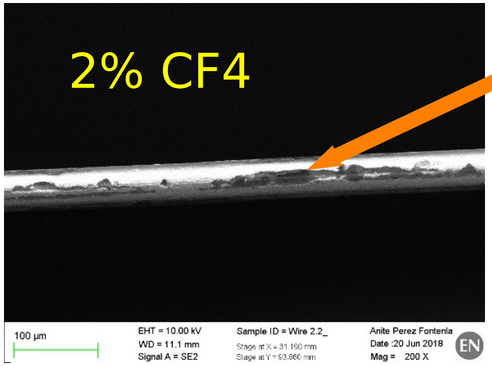


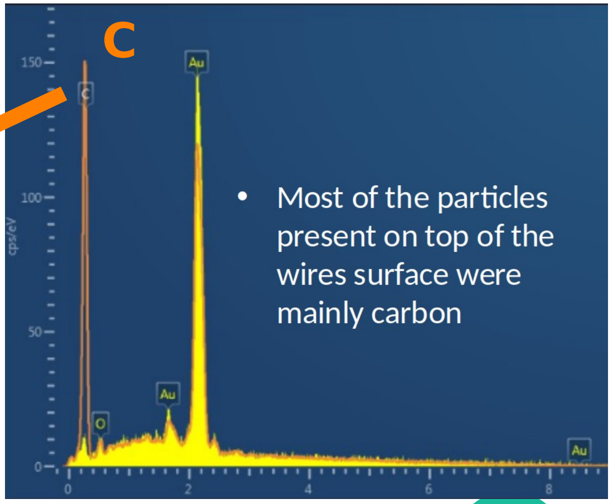


- Recent systematic studies with 10**, 5, 2, 0 %CF4** (open loop gas supply) and small CSC prototypes ("miniCSC") of original design, up to 0.24 C/cm (~ 2 Q(HL-LHC)) – **no performance degradation in all cases but** : **anode wires irradiated with 0 and 2 %CF4 have visible carbon-containing deposits**









F does protect against anode wire ageing and we do need this protection

On the way to a more eco-friendly gas mixture

From the studies with different CF4 fractions (details in Gabriella's talk):

- Preliminarily it seems to be safe to operate the CSC with **5% CF4** – a **reduction of factor two** with respect to the current gas mixture (the studies still ongoing)

- **It is risky to operate the CSC with too low concentration of F-radicals** (as we see with 2% and 0% CF4) – we can not reduce CF4 fraction further but

  we can investigate if there is an eco-friendly replacement for CF4

searches for CF4 replacement

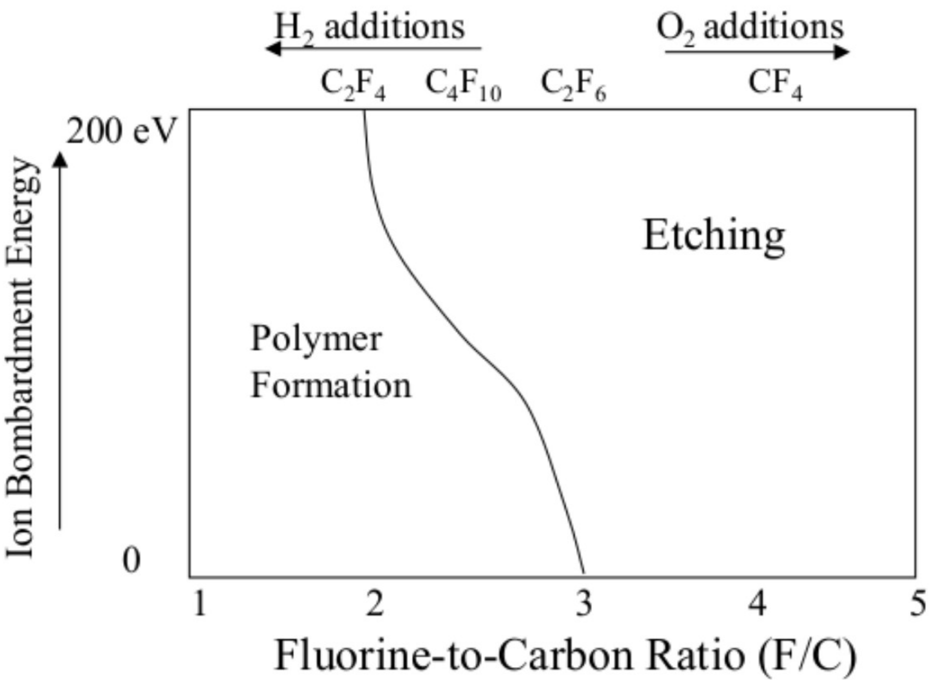
GWP(CF4) ~ 7000

As a potential CF4 replacement we need an F-containing gas

- **with low GWP**
- **that is not hazardous**
- **that prevents ageing in CSC**

where here we mean it has deposit-removal properties…

There are a lot of studies of efficient Si/SiO2/polymer etching in the context of industrial **plasma etching** but they are **not limited to non-hazardous gases**



Philip D. Rack University of Tennessee

However we can use their experience on selecting gases basing on **F/C ratio.** We use it as a hint only, since we do not know if we can apply it directly to an MWPC case

searches for CF4 replacement – general considerations

Searched through ~200 gases requiring ***GWP < O(500):***
perfluocarbons (CxFy), hydrofluorocarbons (CxHyFz), hydrochlorofluorocarbons (CzHyClkFz), hydrofluoroethers (R-O-R')

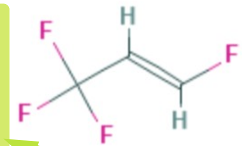
Not examined yet:
fluoroamins, phosphorus halides (mostly toxic…), F-ketons (R2C=O), etc.

Did not consider long molecules : N(C-C)<6

Rejecting flammable and toxic gases, compounds with high boiling point…

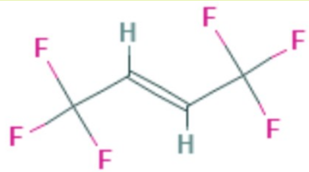
At the moment we stay with four gases of interest:

- **CF3I** (GWP<1) **excluded** in 2015 since too electronegative (+toxic)
- Hydroflueroolefines (HFC with a double C=C bond) :
  - **HFO-1234ze** (GWP=7) intensively studied for RPC
    - does contain F, but F:C ratio is not optimal **(4:3)**

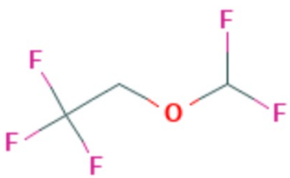


ongoing studies

  - **HFO-1336mzz(E)** (GWP=18)
    - better F:C ratio **(6:4)**
    - but longer molecular chain



- Hydro**chloro**fluerocarbons (HCFC) – HCFC-1233zd(E) – under study by ATLAS-RPC (presented at RPC-2020) - also a replacement of SF6
  - poor F:C ratio (3:3) + chlorine containing
  - probably of low interests for CSC
- Hydroflueroethers (HFE, R-O-R') – **HFE-245fa1 (5:3)** and **HFE-143m (3:2)** GWP~700
  - contain oxygen
  - listed in JINST13 P03012 as being of potential interest for gas detectors

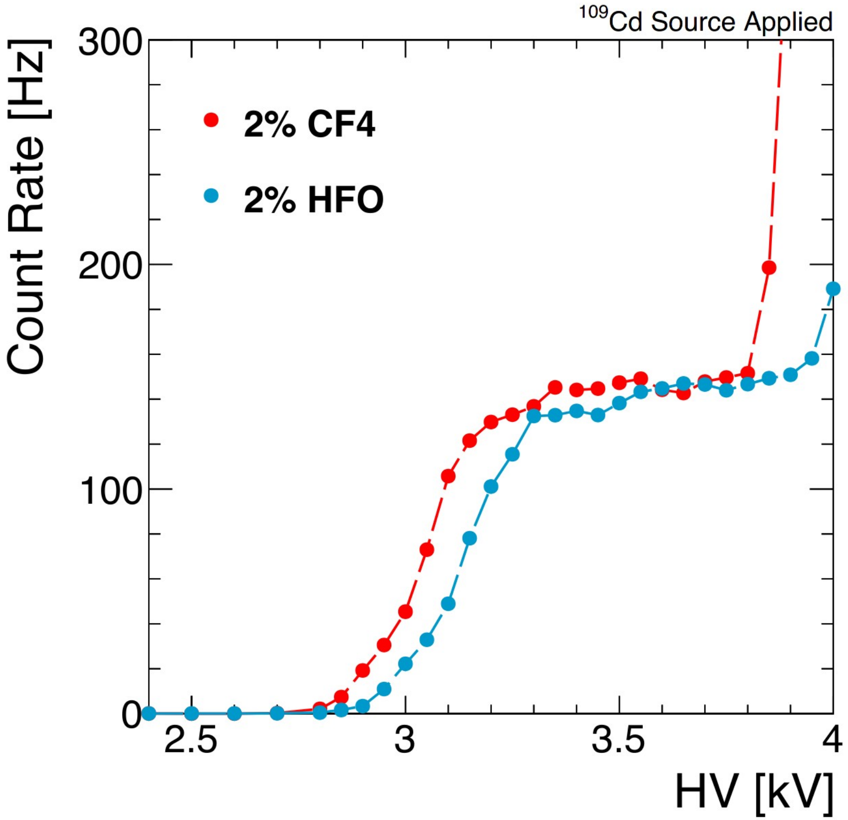


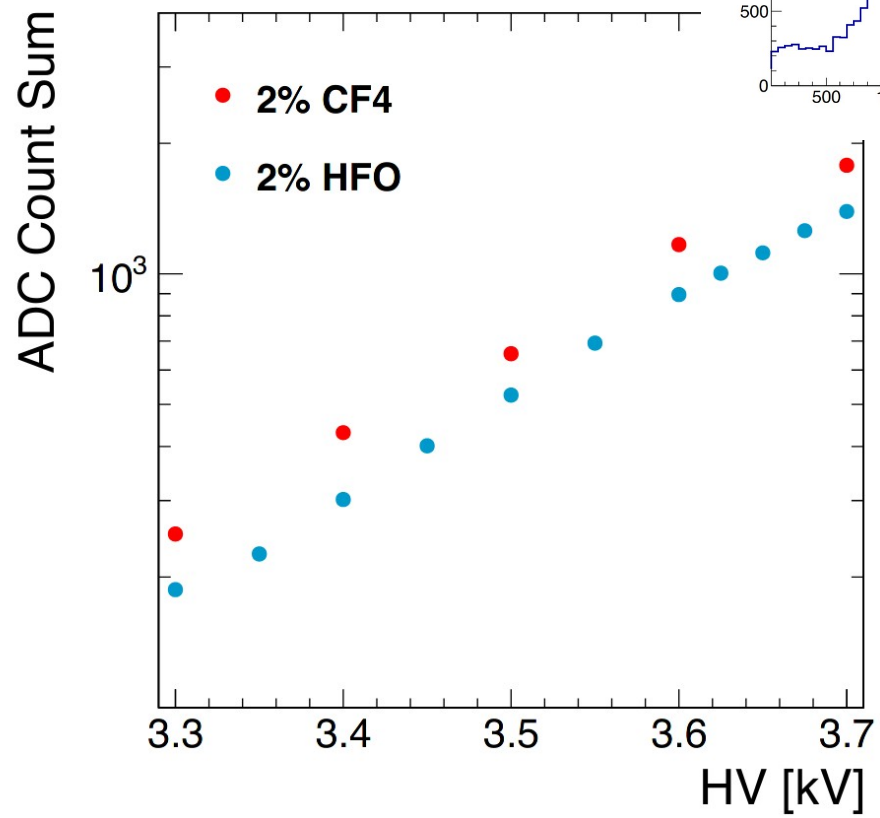
to be considered in more details

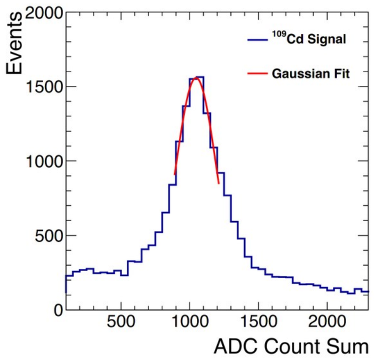
HFO-1234ze – performance studies with miniCSC

Basic detection properties of miniCSC with 2% HFO1234ze:

Measurements with a small prototype, original CSC readout electronics using Cd source: just **~100 V shift** of efficiency plateau – **very promising**







Studies to be continued - more dedicated measurements with different HFO fractions with a miniCSC and finally with an original CSC at test beams

HFO-1234ze – longevity studies

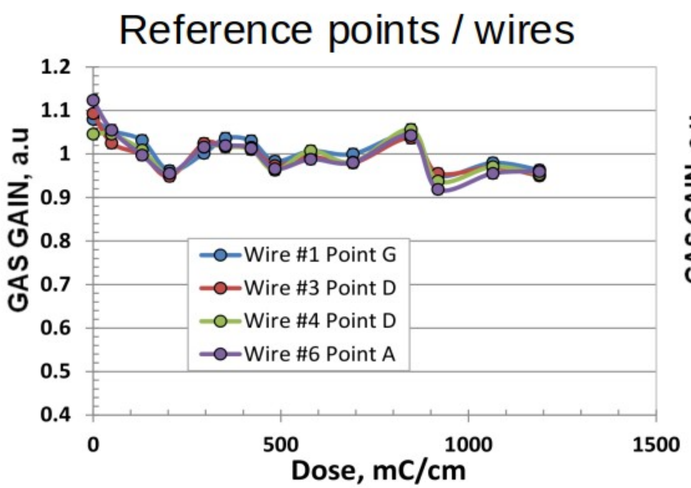
Accelerated longevity studies (PNPI) – "relatively promising"

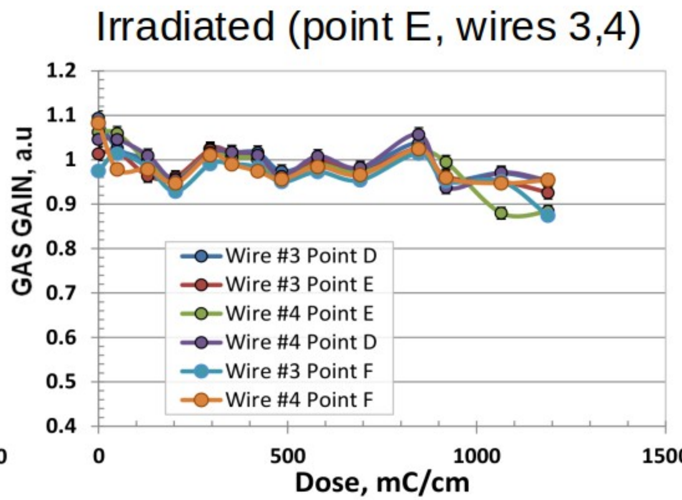
[Longevity studies at PNPI (G.Gavrilov)](#)

Physics of Atomic Nuclei, Volume 83, Issue 10, p.1449-1458 (2020)

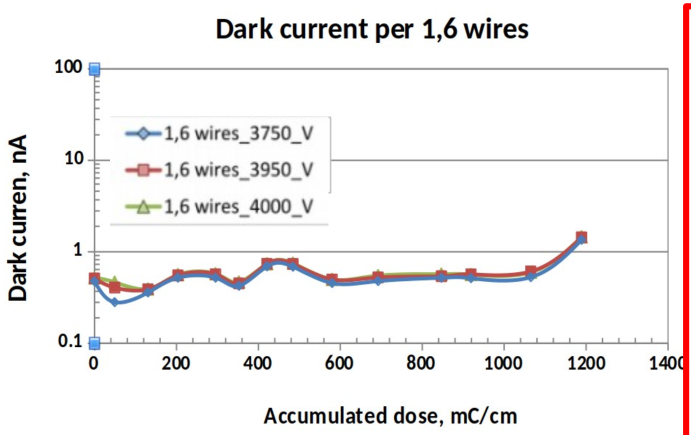
\+ no gain degradation up to 1.2 C/cm

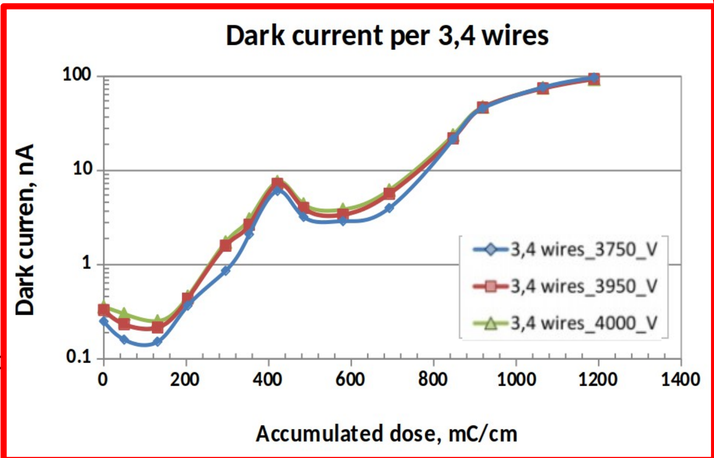
\- significant increase in dark current after 0.6 C/cm





electrode surface analyses are ongoing





Assuming the extra-current coming from the irradiation spot of ~2 cm diameter: **10 nA from 4 cm of the two wires - scaled to 200 m of ME2/1s1 wires give 50 uA** (~ 3 times larger than expected current from the HL-LHC collisions)

Studies will be repeated with a lower ageing acceleration factor

Summary

- Currently four gases are preselected for further studies: **HFO1234ze, HFO-1336mzz(E)** and **HFE-245fa1, HFE-143m**
  - Studies of **HFO1234ze** are ongoing, very preliminary results are relatively promising
    - At the moment it is not obvious if HFO1234ze can be used as a CF4 replacement (long molecular chain, low F/C ratio)
    - More performance and longevity studies are required
      - Performance – b904 (miniCSC) and GIF++ (ME1/1add with muon beam)
      - Longevity – at least one miniCSC longevity test (b904 and/or GIF++), probably several tests with different fractions of HFO
  - If available (not checked yet), **HFO-1336mzz(E), HFE-245fa1** and **HFE-143m** should be studied as well

Backup

systematic studies with different CF4 fractions

miniCSC tests:

10% CF4: irradiated up to ~1.2 C/cm - no gas gain reduction; dark current increase after Q>0.32 C/ cm without degradation of detection performance; no visible deposits on wires

5-0% CF4: irradiated up to ~0.3 C/cm

5% CF4: showed stable performance, no significant visible deposits on wires

0-2% CF4: stable performance, visible darkening of wires - **risky**

0% CF4 in past (*RTV sealant in contact with the gas volume*): **significant deterioration in performance**, significant polymerization on wires. However, longevity tests for that chamber design performed with 10 and 20 %CF4 showed no anode ageing up to at least 12 C/cm

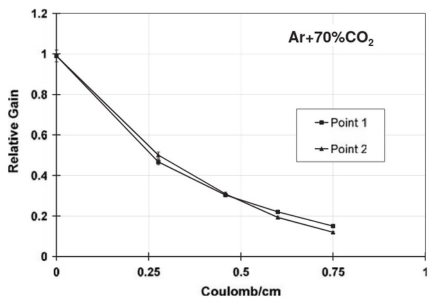
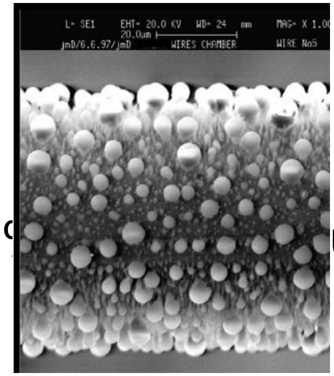


Fig. 13. Gas gain ratio of the test and reference chambers versus accumulated charge at points 1, 2.

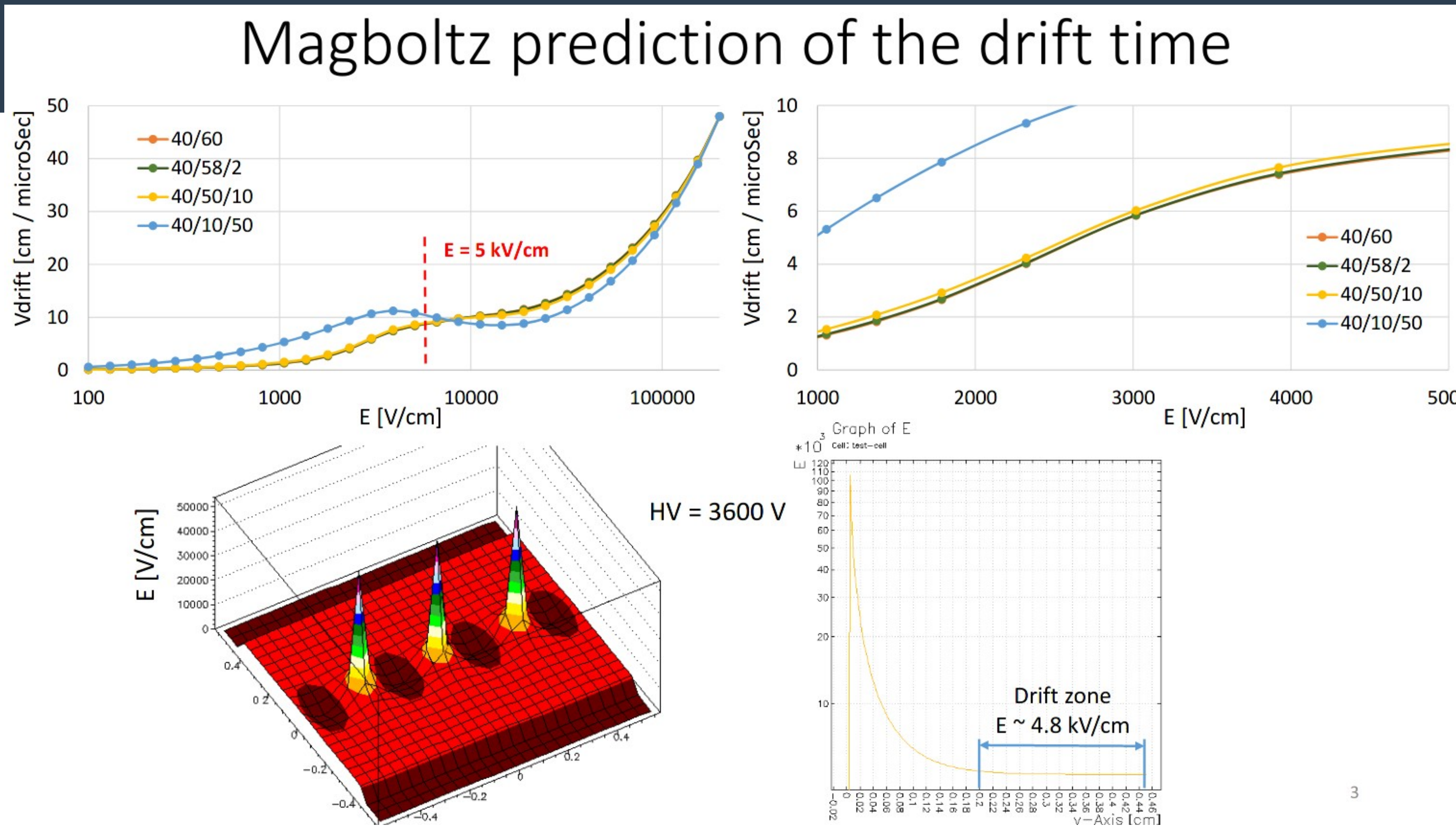


Large CSC tests at GIF++ with 2% C ... 5 ... ure; although some risk):

up to now **+0.27 C/cm** accumulated : ... e

aim to collect at least +0.44 C/cm by mid-2021

Ar/CO2/CF4 : drift velocity



https://indico.cern.ch/event/715570/contributions/2941648/attachments/1620189/2577316/CMS_V_drift.pdf

searches for CF4 replacement

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

  Exception - CF3I

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

			GWP	F:C ratio	remarks
	Carbonyl fluoride	COF2	1	2:1+O	extremely tioxic
	Trifluoroiodomethane	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

- **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

searches for CF4 replacement

			GWP	F:C ratio	remarks
HFC-1132a	Vinylidene fluoride	CH2=CF2	<1	2:2	ExtF, toxic
HFC-1141	Vinyl fluoride	CH2=CHF	<1	1:2	ExtF
HFC-1225ye	1,2,3,3,3-Pentafluoropropene	CF3CF=CHF	<1	5:3	Irritant
HFC-1234yf	2,3,3,3-Tetrafluoroprop-1-ene	CH2=CF-CF3	4	4:3	F
HFC-1234ze(E)	trans-1,3,3,3-Tetrafluoroprop-1-ene	CHF=CH-CF3 (E)	7	**4:3**	
HFC-1243zf	3,3,3-Trifluoropropene	CF3CH=CH2	<1	3:3	F, toxic
HFC-1336mzz(Z)	cis-1,1,1,4,4,4-Hexafluorobut-2-ene (CAS:692-49-9)	CF3-CH=CH-CF3 (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)	CF3-CH=CH-CF3 (E)	18	**6:4**	**no hazards, pb=8°C;**
HFC-1345zfc	3,3,4,4,4-Pentafluorobut-1-ene	C2F5-CH=CH2	<1	5:4	F
HCFC-1224yd(Z)	cis-1-Chloro-2,3,3,3-tetrafluoroprop-1-ene	CHCl=CF-CF3 (Z)	1	4:3+**Cl**	no hazard info; Ashai Glass (Japan)
HCFC-1233xf	2-Chloro-3,3,3-trifluoroprop-1-ene	CH2=CCl-CF	1	1:3+**Cl**	F, irritant
HCFC-1233zd (E)	trans-1-Chloro-3,3,3-trifluoroprop-1-ene	CHCl=CH-CF3 (E)	4.5	3:3+**Cl**	no hasards; **ATL-RPC**
HCFE-235da2	Isoflurane	CHF2-O-CHCl-CF3	350	5:3+**Cl**+O	toxic

HFO (a double bond)

HCFC

Increasing chain length

searches for CF4 replacement

HFE: mostly have a high boiling point

The two ethers from the JINST publication have GWP slightly above the cut (500) but still ~10 times better than CF4

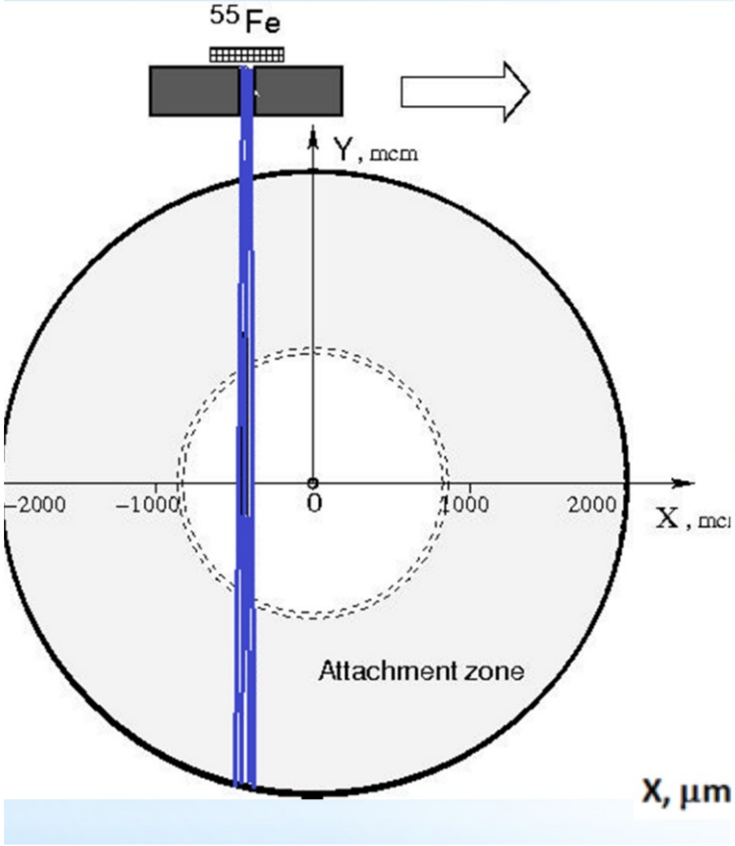
HFE-143m		CF3-O-CH3	750	**3:2+O**	**JINST13 P03012; bp= -24°C**
HFE-236fa	CAS: 20193-67-3	CF3-CH2-O-CF3	487	**6:3+O**	bp=62°C
HFE-245fa1	CAS: 84011-15-4	CHF2-CH2-O-CF3	286	**5:3+O**	bp=26°C
HFE-245mc		CF3-CF2-O-CH3	622	**5:3+O**	**JINST13 P03012 ; bp=5°C**
HFE-254cb2	CAS: 425-88-7	CH3-O-CF2-CHF2	359	4:3+O	HiF; irritant
HFE-263fb2	CAS: 460-43-5	CF3-CH2-O-CH3	11	3:3+O	no hazard info; bp=31°C;
HFE-338mmz1	CAS: 26103-08-2	(CF3)2CH-O-CHF2	380	**8:4+O**	bp=40°C;
HFE-347mcf2	CAS: 171182-95-9	CHF2-CH2-O-CF2-CF3	374	**7:4+O**	bp=50°C;
HFE-347mmy1	CAS: 22052-84-2	(CF3)2CF-O-CH3	343	**7:4+O**	Irrititant; bp=29°C;
HFE-347mmz1	(Sevoflurane)	CH2F-O-CH(CF3)2	216	**7:4+O**	bp=56°C;
HFE-356mec3	CAS: 382-34-3	CH3-O-CF2-CHF-CF3	101	6:4+O	F, Irritant; bp=53°C;
HFE-356mm1	CAS: 13171-18-1	(CF3)2CH-O-CH3	27	6:4+O	F?. Irritant?; bp=50°C;
HFE-356pcc3	CAS: 160620-20-2	CH3-O-CF2-CF2-CHF2	110	6:4+O	bp=68°C;
HFE-356pcf2	CAS: 50807-77-7	CHF2-CH2-O-CF2-CHF2	265	6:4+O	bp=74°C;
HFE-365mcf3	CAS: 378-16-5	CF3-CF2-CH2-O-CH3	11	5:4+O	F; bp=46°C;

HFE

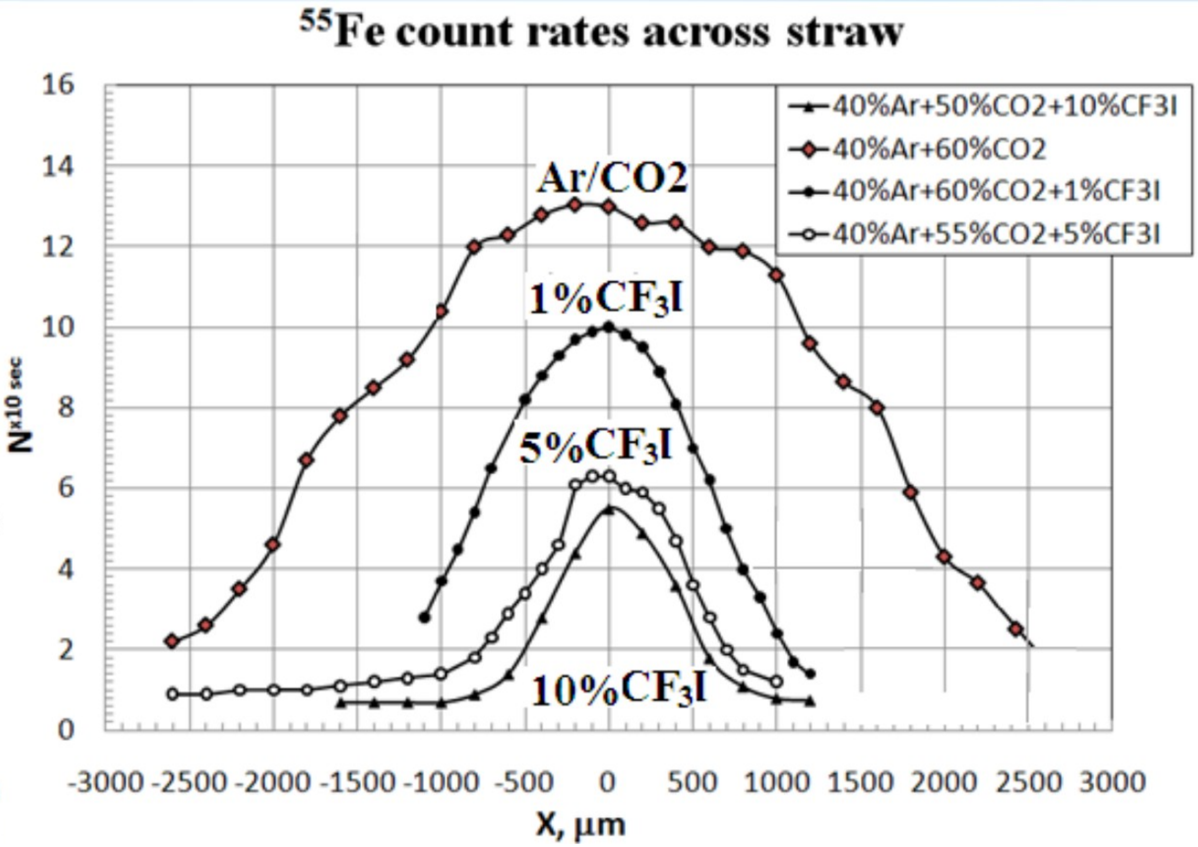
Increasing chain length

In total only 4 gases of potential interest

CF3I



55 Fe
Y, mcm
-2000
-1000
0
1000
2000
X, mc
Attachment zone
X, µm



55Fe count rates across straw
40%Ar+50%CO2+10%CF3I
40%Ar+60%CO2
40%Ar+60%CO2+1%CF3I
40%Ar+55%CO2+5%CF3I
Ar/CO2
1%CF3I
5%CF3I
10%CF3I
N x10 sec
X, µm