

dRICH radiator gas

Fulvio Tassarotto

C_4F_{10} - COMPASS RICH radiator gas

C_2F_6 choice for ePIC

How much gas is needed?

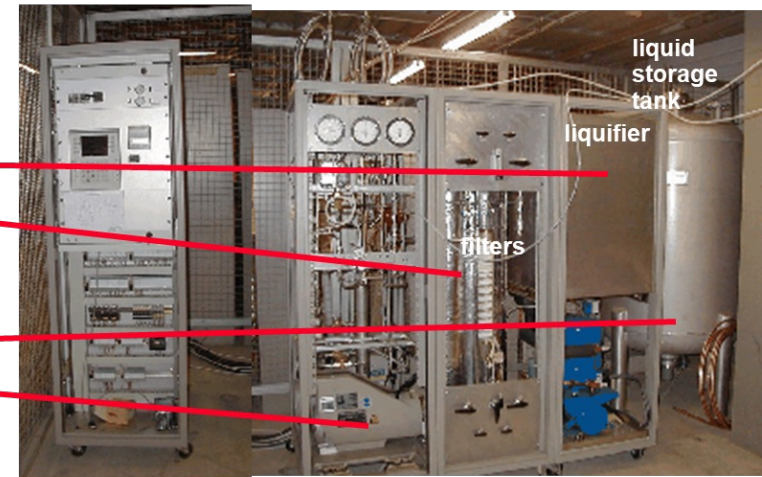
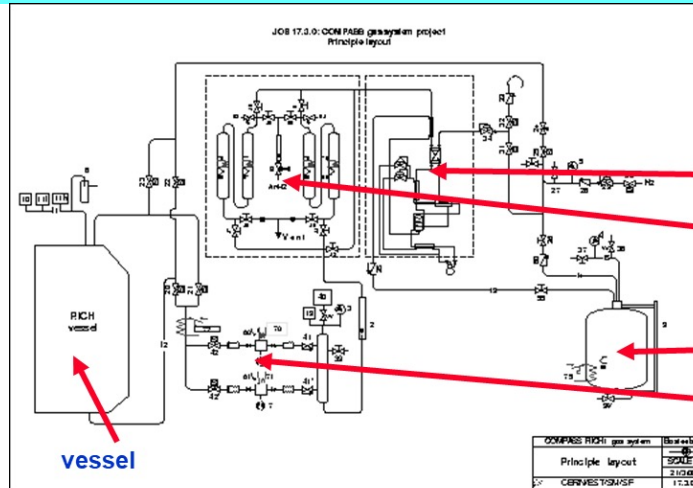
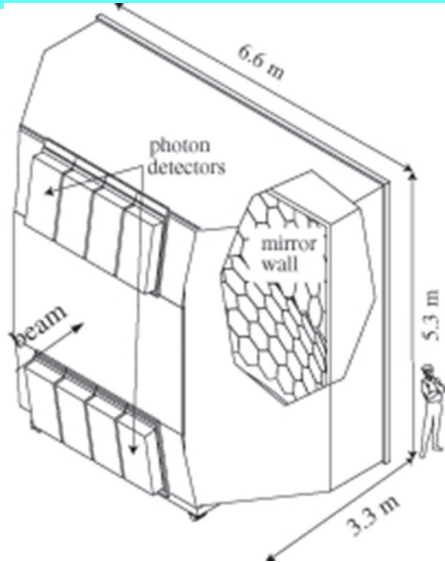
GWP and NOVECs

Alternative radiator gas options

PFAS ban discussion

Pressurized argon

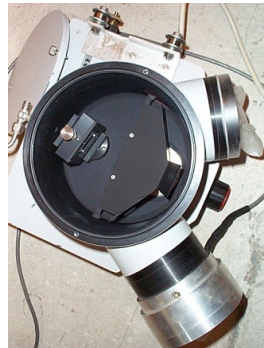
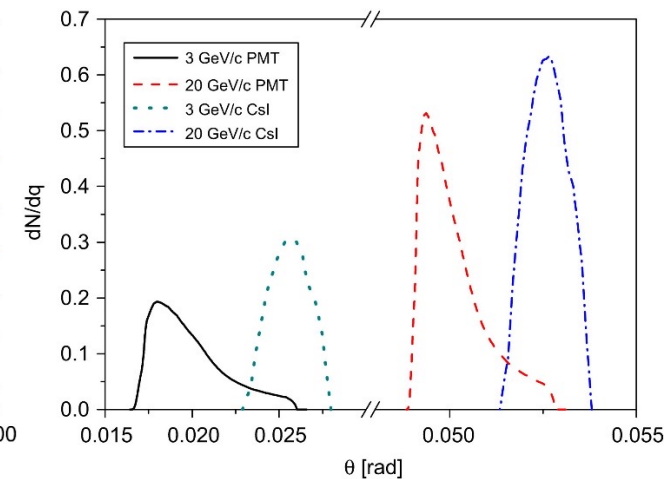
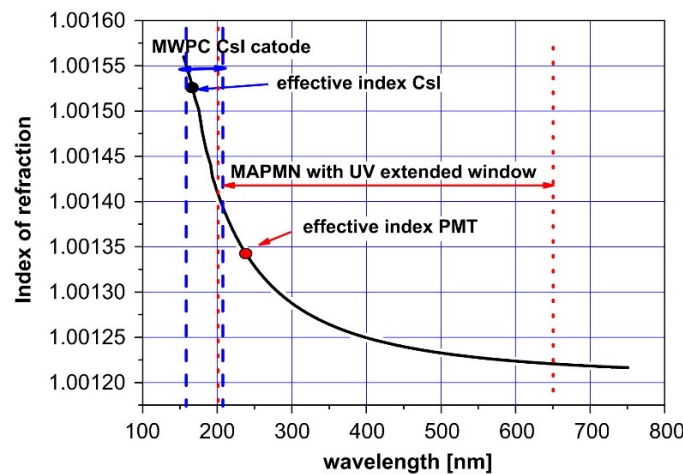
COMPASS radiator gas system

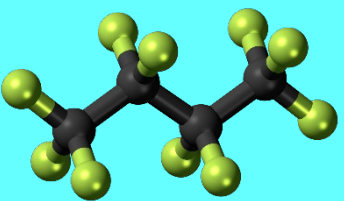


PLC and electrical installation

compressors

Gas choice: good refractive index, high photon yield, low chromaticity.
 Continuous gas circulation of $\sim 80 \text{ m}^3$ radiator gas. Relative P constant $\pm 0.1 \text{ mbar}$ w.r.t atmospheric.
 Gas filtering (remove H_2O , O_2). Filling recovering C_4F_{10} Closed loop system. Sampling for analysis





COMPASS radiator gas: C₄F₁₀

For large quantities:

3M(*): performance fluid PF-5040

- Production stopped around 2010 (in the following few years they have sold out what remaining in stock)
- Produced in different plants around the world
- Observed over years (also going back to DELPHI experience): different amount and nature of impurities
- Used in COMPASS till 2017

SPECIFICATIONS:
NOTE: These are introductory specifications based upon limited production data and are subject to change.

Property	Test Method	Unit	Lower Limit	Target	Upper Limit
Perfluorobutane	135.266	%mole	99.0	-	-
Water	300.201	ppm	-	-	10.0
High Boiling Impurities	1.13.5.9	%	-	-	0.05
Comment: (volume) Residue	1.13.5.9	ug/ml	-	-	100.0
Free Fluoride	53.23	ppm	-	-	0.14

(*): Minnesota Mining and Manufacturing Company, 3M Center, St. Paul, MN, USA

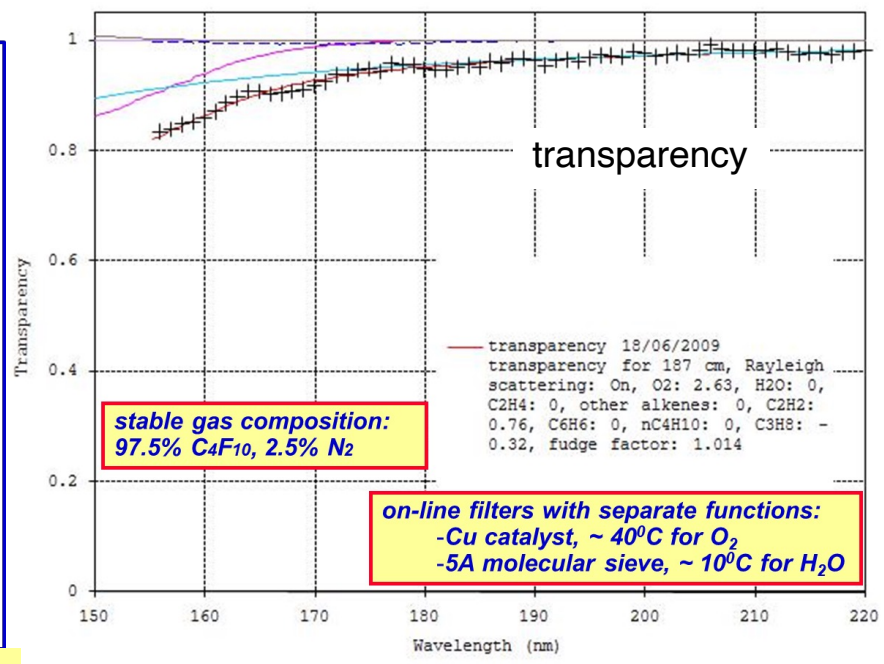
F2Chemicals(*): perfluorobutane, QS25

- Used in COMPASS after 2017

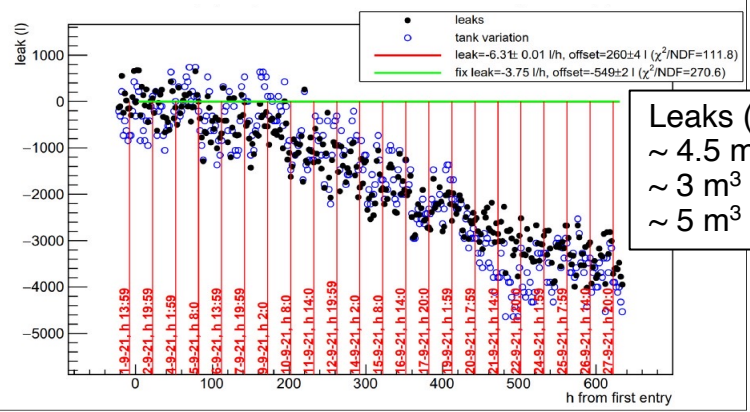
Assay (excluding air)		
Total Perfluorobutane	98 % v/v min	FC-40-011
Total impurities, by GLC	2 % v/v max	FC-40-011
Related Perfluorinated compounds		
Perfluoropropane	1% v/v max	FC-40-011
Perfluoromethane	0.5 % v/v max	FC-40-011
Perfluoroethane	0.5 % v/v max	FC-40-011
Perfluorocyclobutane	0.5 % v/v max	FC-40-011
Each single unknown	0.5 % area max	FC-40-011
Others		
Air	0.5 % v/v max	FC-40-011
Acetone	100 ppm w/w max	FC-40-012

Note - Analysis to be performed on the liquid phase.

(*): F2 Chemicals LTD, Lea Lane, Le...



Vessel Leakage (liters) from 31-8-2021 to 28-9-2021 : -6.31 l/h

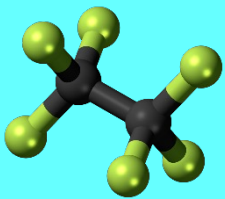


Improved cleaning procedure efficiency
0.7 → 0.95

Leaks (~6 months of operation/year)
~ 4.5 m³ month → 25 m³ data taking year
~ 3 m³ from the filtering system
~ 5 m³ from the recovery procedure

COMPASS consumption:
~350 kg/y

Producer: F2 chemicals
available on stock: 550 kg
old price: 199 £/kg
New production requires:
- a minimal order
- from 6 months to 1 y



ePIC dRICH possible radiator gas: C_2F_6

F2 Chemicals does not produce C_2F_6 ;
They produce C_3F_8
(~250 t/y)
price: ~ 38 £/kg

Several distributors contacted:
availability confirmed by two:

- SIAD S.p.A.
- Resonac Europe GmbH

SIAD S.p.A. offers:
 C_2F_6 (R116) purity 99,999%
Bottles of 50 l, (52 kg each)
Stainless steel DIN-6 conn.
Price: 3172 Euro/bottle
Delivery time: 6 weeks from order

Yearly leaks are difficult to estimate:

- Filling and recovery operations 6%
- Filtering and maintenance 3%
- **Leaks 10%**
- Sampling, analysis, etc. 2%

CERN new gas systems qualification standard:

Target Leak flow at reference conditions	<1*10 ⁻³ STD cc/s
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**Tentative estimate for the cost of a “leakless”
system built at CERN for C_2F_6 :**
~250 kCHF

30 kg/y emission → large environmental impact: ~300 tCO₂e/y

From Marco Contalbrigo: “assume volume = 20 m³”

C_2F_6 density: 5,73 kg/m³ → 114 kg

Initial minimal quantity: ~200 kg

500 kg could be enough for 10 y of operation

Just a very first estimate to start a discussion

... these numbers will certainly change ...

GWP and CERN emissions

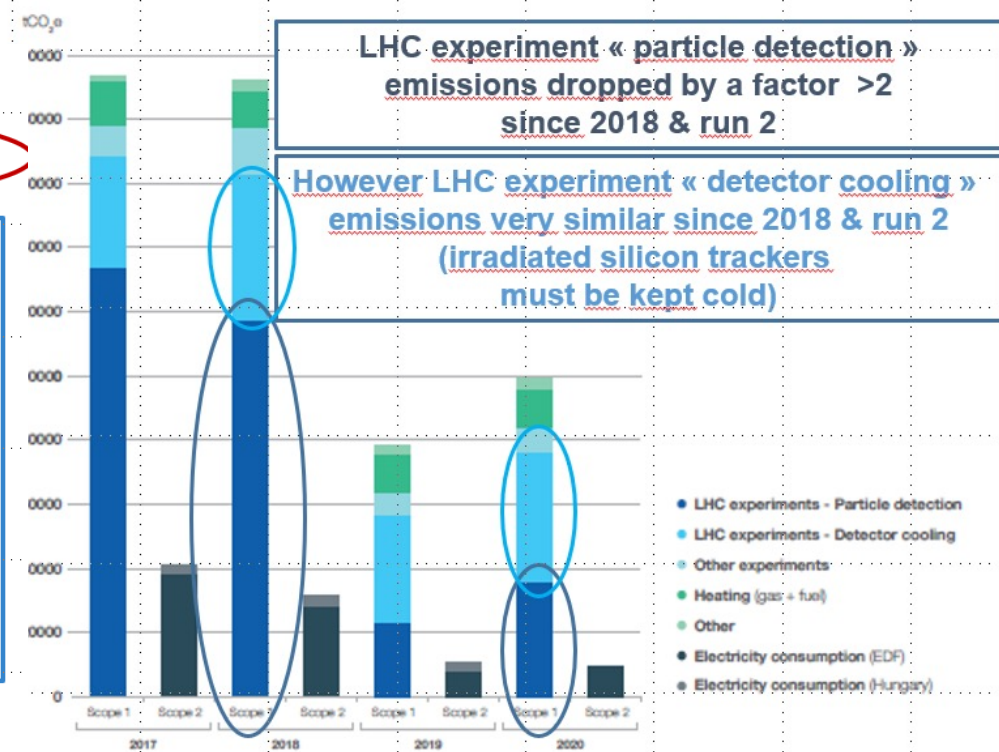
https://e-publishing.cern.ch/index.php/CERN_Environment_Report/issue/view/102;

GROUP	GASES	tCO ₂ e 2019	tCO ₂ e 2020
PF6	CF ₄ , C ₂ F ₆ , C ₃ F ₈ , C ₄ F ₁₀ , C ₅ F ₁₂ , C ₆ F ₁₄	43277	45678

- CF₄ LHCb RICH2: **GWP = ~ 4880_{CO2}* [16]**
 - C₂F₆ ATLAS evap cooling (potential use): **GWP = ~ 11000_{CO2}***
 - C₃F₈ F2 Chemicals, Astor, ATLAS evap cooling: **GWP = ~ 8900_{CO2}***
 - C₄F₁₀ LHCb RICH1; COMPASS RICH: **GWP = ~ 8500_{CO2}***
 - C₅F₁₂ PP50: **GWP = ~ 8500_{CO2}***
 - C₆F₁₄ PP1, F2 Chemicals: Liquid cooling, many expts: **GWP = ~ 8000_{CO2}***
- For some perspective: SF6 GWP = ~ 23000_{CO2}***
- See references: 100_{yr} (average of 2nd, 4th & 5th assessment reports; AR2,4,5)
 - https://www.ghgprotocol.org/sites/default/files/ghgp/Global-Warming-Potential-Values%20%28Feb%2016%202016%29_1.pdf

Which NOVEC®? What molecular structure: C₆F₁₂O (GWP = 0)?
 Extremely unfair and deceptive to group NOVEC
 on the same line as SF₆ (GWP = 23000)

G. Hallewell ECFA TF-4 Meeting May16-17th 2023



RIN SCOPE 1 AND SCOPE 2 EMISSIONS FOR 2017-2020 BY CATEGORY. *ier in dudes air conditioning, electrical insulation, emergency generators and CERN vehicle fleet fuel consumption; Emission factors for electricity: F Bilan des émissions de GES 2002-2020 for EDF and Bilan Carbone® V8 for Hungary.*

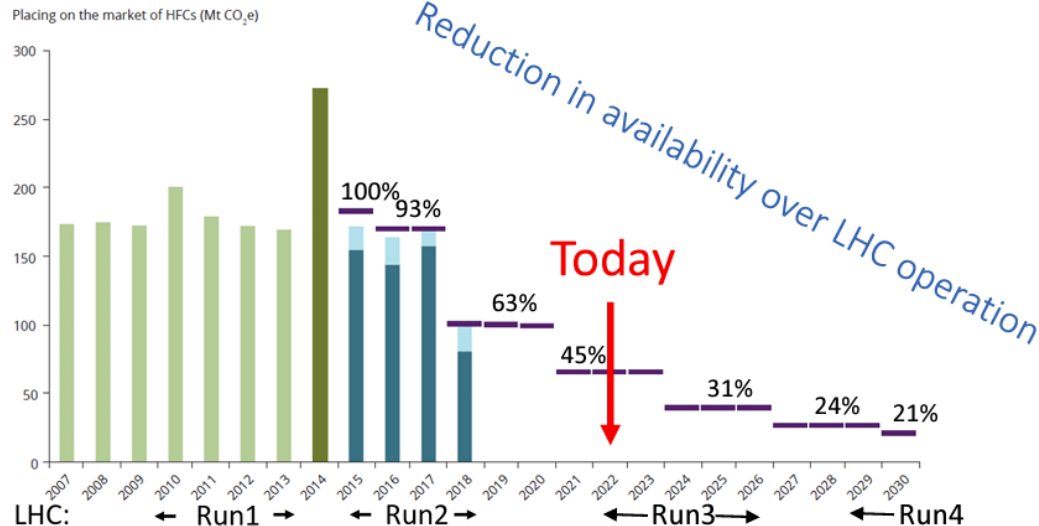
G; Hallewell: RICH 2022, Edinburgh : Sept 12-16, 2022

The case of HFC

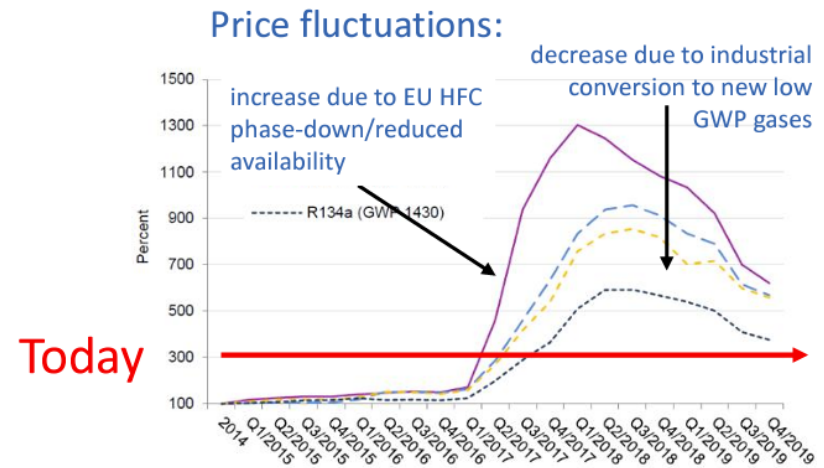
Due to the environmental risk, “**F-gas regulations**” started to appear. For example, the EU517/2014 is:

- **Limiting** the total amount of the most important F-gases that can be sold from 2015 onwards. By 2030, it limits the use to 1/5 of 2014 sales.
- **Banning** the use of F-gases in new equipment where less harmful alternatives are available.
- **Preventing** emissions of F-gases from existing equipment by requiring checks, proper servicing and recovery of gases.

Figure ES.1 Progress of the EU HFC phase-down



HFC phase down: effects on HFC availability and prices



Sources: European Environment Agency, Fluorinated greenhouse gases 2019 report
 Öko Recherche report, March 2020 J. Kleinschmidt et al.

Roberto Guida, “Search for the ECO-friendly gas-mixtures for the muon detectors at LHC and beyond” 29/05/2023

Alternative gases: C₄F₈O

Footer

BTeV study: optics good – GWP not



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 Nuclear Instruments and Methods in Physics Research A 553 (2005) 339–344



Beam test of a C₄F₈O-MAPMT RICH prototype

Tomasz Skwarnicki*

Department of Physics, Syracuse University, Syracuse, NY 13244, USA

Available online 2 September 2005
 On behalf of the BTeV RICH Group

Abstract

We present results from the first beam test of the gaseous BTeV RICH. A new gas, C₄F₈O, is used as Cherenkov radiator for the first time. A new generation of the MAPMT tubes from Hamamatsu, R8900-M16, are used as the photon detector.
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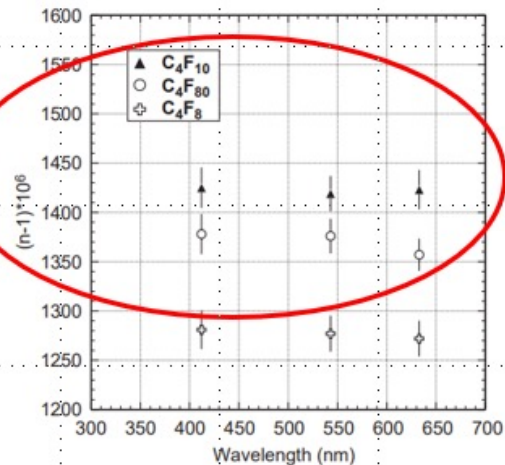
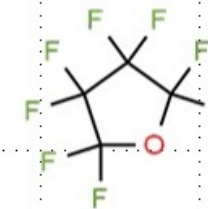
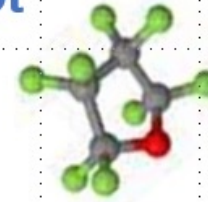


Fig. 5. Measurements of refraction indices of various gases as a function of laser light wavelength.

We then filled the gas tank with C₄F₈O. This is a replacement gas for C₄F₁₀, which was previously used in many RICH detector. The industrial process at 3M yielding C₄F₁₀ as a byproduct was recently discontinued. Even though some stockpiles still exist, the prices have gone up and long-term availability is highly questionable. The C₄F₈O gas (octafluorotetrahydrofuran) has been widely in use by the semiconductor industry for plasma etching and cleaning CVD chambers since 1999. Since this is the first time this gas is used as a Cherenkov radiator, we include some basic information about this substance. It is about 10 times heavier than air (9.19 g/L at 21 °C, 1 atm; 1.52 g/mL as liquid). Matheson TRI-GAS Material Safety Data Sheets give -0.8 °C for its boiling point, whereas American Chemical Society gives a slightly lower

number: -5.5 °C. The break-up temperature for the molecule is 225 °C. It is not a poison. It is non-explosive, colorless and odorless. It is chemically stable and non-reactive except with alkali halide metals (Sodium, Potassium). According to the manufacturer it can pick-up and transport oils. Contact with organic materials should be minimized. It is produced by 3M. According to the distributor² the gas is 99.6% pure. The impurities consist mostly of the isomer of the main molecule (the latter has a cyclic structure: -CF₂-CF₂-O-CF₂-CF₂-) and other perfluorocarbons (freons). Non-perfluorocarbons are less than 0.05% of the volume. We measured the refraction index of C₄F₈O, C₄F₁₀ and C₄F₈ at 3 visible wavelengths using lasers and Michelson interferometry. The results are shown in Fig. 5. The refraction index of C₄F₈O is only slightly smaller than that of C₄F₁₀.

The test-beam data with C₄F₈O as radiator were taken over 2 days. The air contamination varied between 4% and 8%, as measured by weighing the gas collected at the exhaust located on the top of the tank. The pressure/temperature ratio was stable within 1%. We took 10 separate runs with

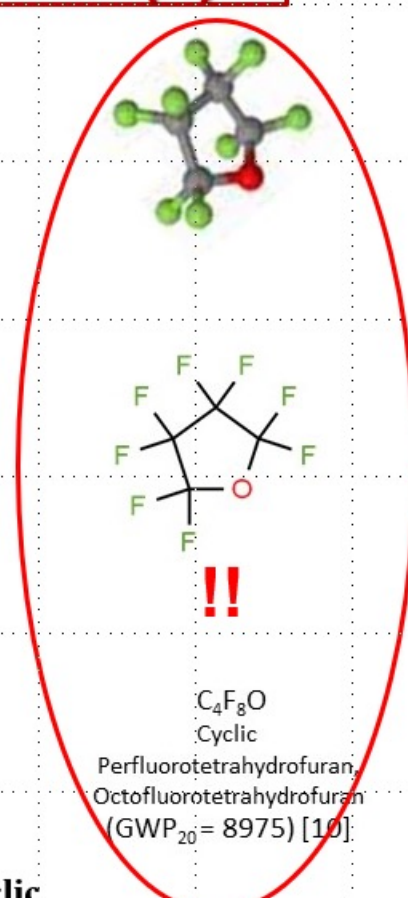
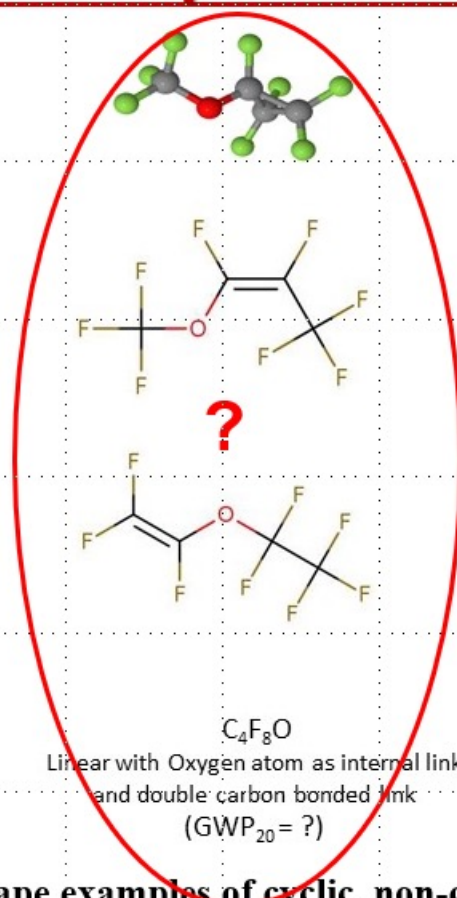
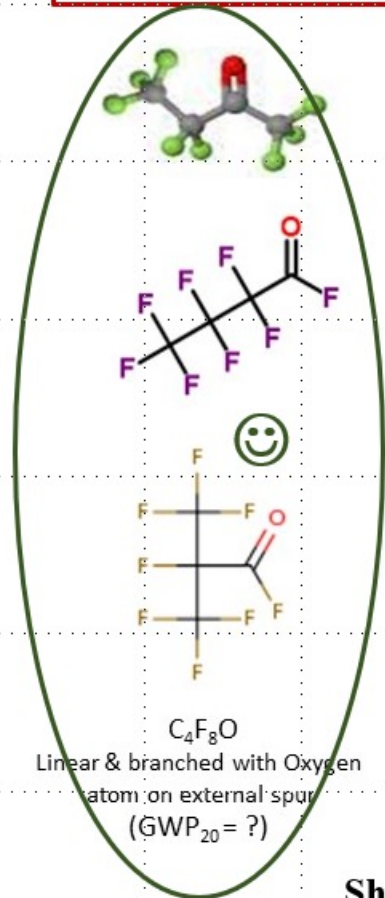


In conclusion, the C₄F₈O gas was used as Cherenkov radiator for the first time and proved to be a suitable replacement for C₄F₁₀. The new generation of MAPMTs from Hamamatsu (R8900-M16) with a high fraction of active area was tested together with a newly developed Va_MAPMT ASIC and performed according to expectations.

I would like to acknowledge the other members of the BTeV RICH group for their contributions to the results presented in this article: M. Artuso, S. Blusk, C. Boulahouache, J. Butt, H. Cease, O. Dorjkhaidav, A. Kanan, N. Menaa, R. Mountain, H. Muramatsu, R. Nandakumar, L. Redjimi, K. Randrianarivony, S. Stone, R. Sia, J. Wang and H. Zhang.

Alternative radiator gases

Molecular shapes and GWP (2)

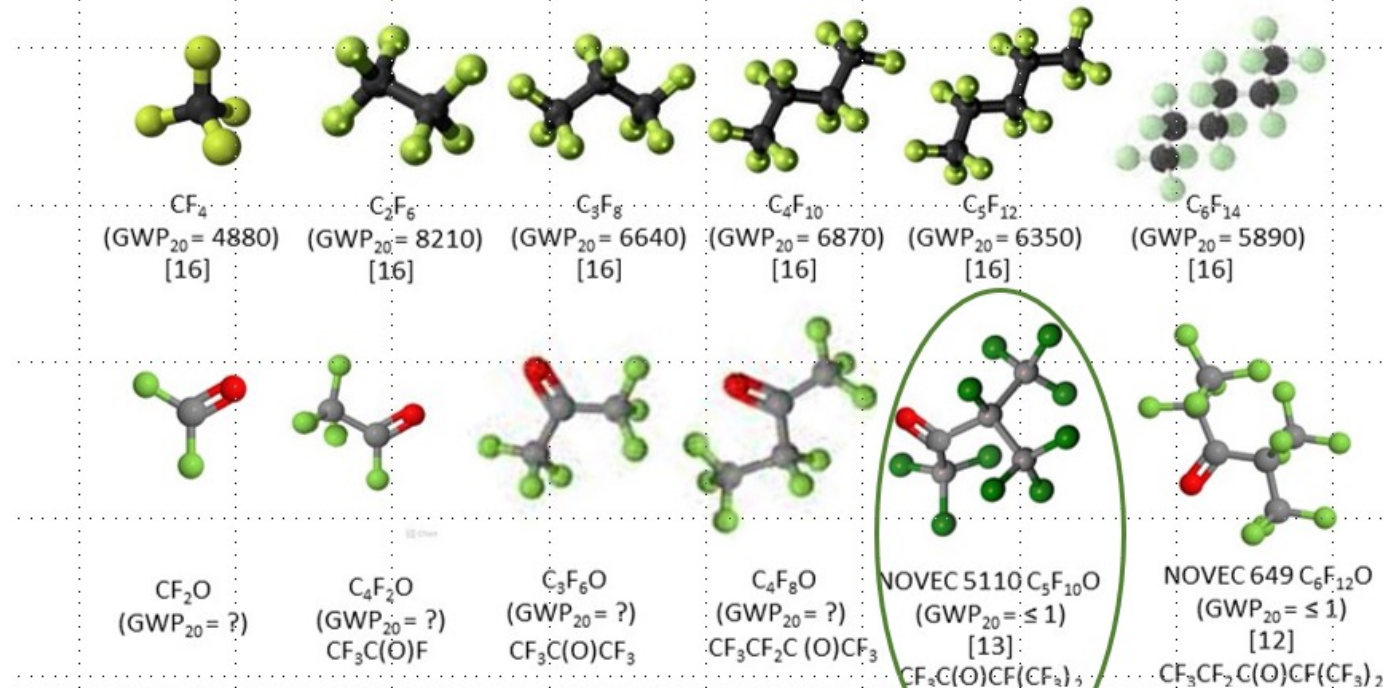


Shape examples of cyclic, non-cyclic & non-cyclic double carbon-bonded C4F8O isomers refs at end.

G. Hallewell: GasRad GWP: ECFA TF-4 Meeting May16-17th 2023

Alternative radiator gases

Molecular shapes and GWP (1)



Upper: molecular shapes of SFCs, including common gaseous Cherenkov radiators

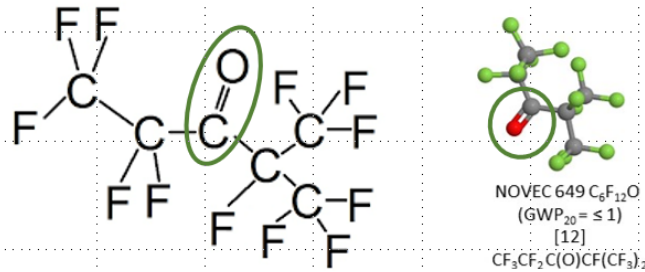
Lower: shapes of some non-cyclic C_nF_{2n}O analogues

(20-year GWPs noted where known – refs at end)

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Alternative gas mixtures

Q: But What gives NOVEC 649/1230 (a spurred-Oxygen fluoro-ketone) its low GWP?



A: Structure!: a double-bonded oxygen atom on a peripheral spur of the molecule

This fluoro-ketone configuration is:
 $CF_3CF_2C(O)CF(CF_3)_2$

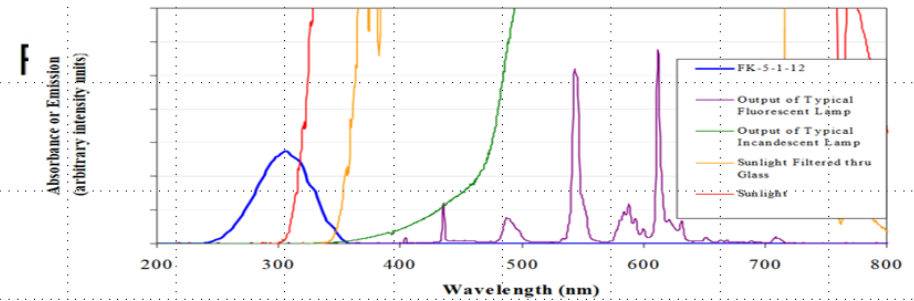
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Q: What gives NOVEC 649/1230 its low GWP?

https://www.nist.gov/system/files/documents/el/fire_research/R0301570.pdf [15]

Figure 3. UV Absorption of FK-5-1-12 Compared to Light Sources



Scission by UV photons of λ around 300 nm
In the atmosphere (low pressure, high UV): the fragments do not reassociate* into saturated fluorocarbons of the type $C_nF_{(2n+2)}$ (which would have high GWP)

*The Environmental Impact of CFC Replacements HFCs and HCFCs
T. WALLINGTON et al *Environ. Sci. Technol.* 1994(28)7 320A
<https://doi.org/10.1021/es00056a714>

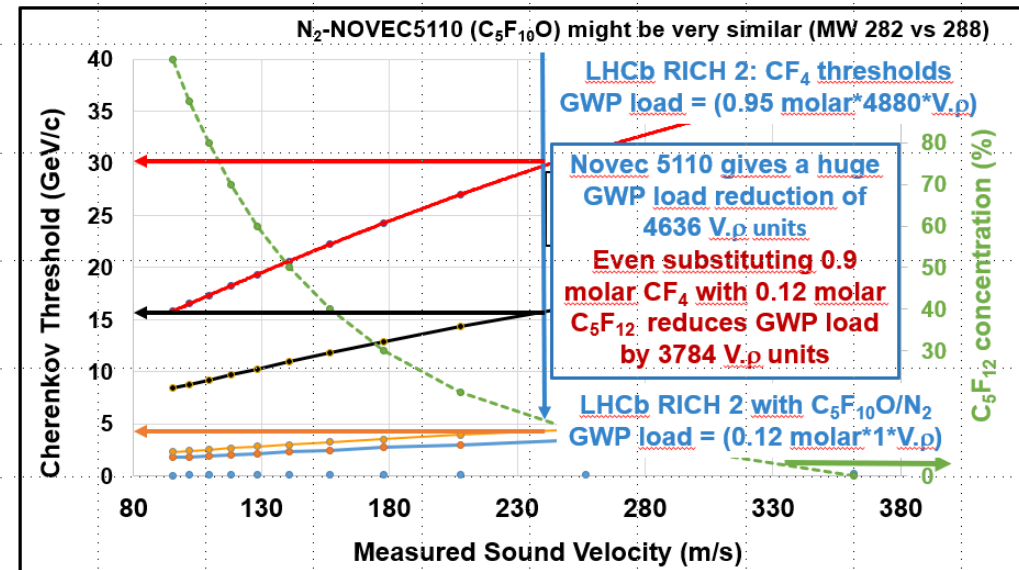
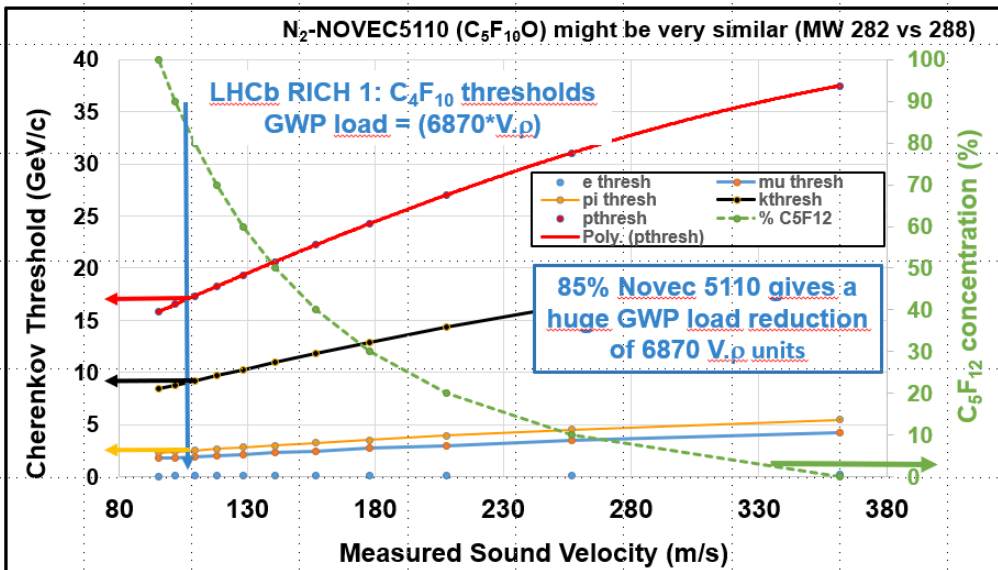
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Blending NOVEC 5110 with N₂

Cherenkov threshold in C₅F₁₂/N₂ mixtures and GWP load comparison with LHCb RICH1 (new vol.?)

Cherenkov threshold in C₅F₁₂/N₂ mixtures and GWP load comparison with LHCb RICH2 (new vol.?)



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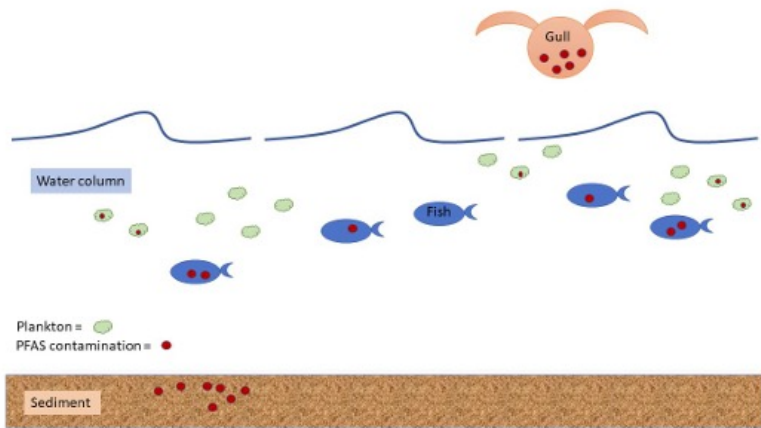
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PFAS: per-(poly-)fluoroalkyl substances

PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group (-CF₃) or a perfluorinated methylene group (-CF₂-) is a PFAS

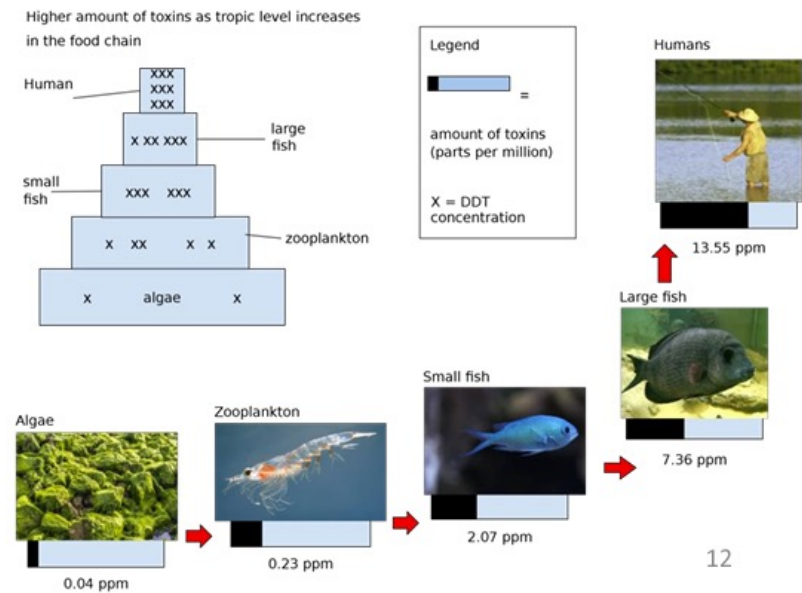
PFASs play a key economic role for companies such as DuPont, 3M, and W. L. Gore & Associates because they are used in emulsion polymerization to produce fluoropolymers. They have two main markets: a \$1 billion annual market for use in stain repellents, and a \$100 million annual market for use in polishes, paints, and coatings. In 2022, 3M announced that it will end PFAS production by 2025.

Bioaccumulation and biomagnification



29/05/2023

Belgrade workshop



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Roberto Guida, "Search for the ECO-friendly gas-mixtures for the muon detectors at LHC and beyond" 29/05/2023

PFAS: per-(poly-)fluoroalkyl substances

- The restriction was proposed by Germany, The Netherlands, Sweden, Denmark and Norway for the EU.
- It aims to be biggest chemical ban out of health considerations.
- **Imports will also be considered in the restriction.**



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PFAS: per-(poly-)fluoroalkyl substances

- There are 2 Restriction options:
 - Full ban; 18 months after entry into force
 - Full ban; 18 months after entry into force with time-limited derogations for specific use-cases.

Basis for derogations

18 months after Eif	18 months + 5 years	18 months + 12 years
Alternatives exist	Sufficiently strong evidence that technically and economically feasible alternatives are in development	Sufficiently strong evidence that technically and economically feasible alternatives are not available in near future (R&D)
No or not sufficiently strong evidence that alternatives are not available	Sufficiently strong evidence that alternatives exist, but not available in sufficient quantities and/or cannot be implemented by company before transition period ends	Certification or regulatory approval of PFAS-free alternatives cannot Be achieved within a 5-year derogation period

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Chromaticity

If we work near the chromatic limit, the choice is limited.

The best gas is helium, at the appropriate pressure.

For an intuitive comparison:

	He	Ne	Ar	Kr	Xe	C2F6	C4F10
(n-1)@300 nm	35.54	67.6	295.44	455.68	762.26	850	1280
(n-1)@600 nm	34.86	66.1	282	427.23	688.6	820	1220
<u>Theta@300 nm</u>	8.4309	11.6276	24.308	30.1887	39.0451	41.2311	50.5964
<u>Theta@300 nm</u>	8.34985	11.4978	23.7487	29.2311	37.1106	40.4969	49.3964
Delta Theta	0.08105	0.12973	0.55934	0.95759	1.93446	0.73414	1.20009
(Delta Theta)/Theta	0.00961	0.01116	0.02301	0.03172	0.04954	0.01781	0.02372

$$\Delta\theta = \theta_{\check{c}}(\lambda=300\text{nm}) - \theta_{\check{c}}(\lambda=600\text{nm}) \quad ; \quad \rho = \Delta\theta/\theta_{\check{c}}(\lambda=300\text{nm})$$

$$\rho_{\text{He}} = 0.96\% \quad ; \quad \rho_{\text{Ne}} = 1.1\% \quad ; \quad \rho_{\text{Ar}} = 2.3\% \quad ; \quad \rho_{\text{Kr}} = 3.2\% \quad ; \quad \rho_{\text{Xe}} = 4.9\% \quad ;$$

$$\rho_{\text{C2F6}} = 1.8\% \quad ; \quad \rho_{\text{C4F10}} = 2.4\% \quad ;$$

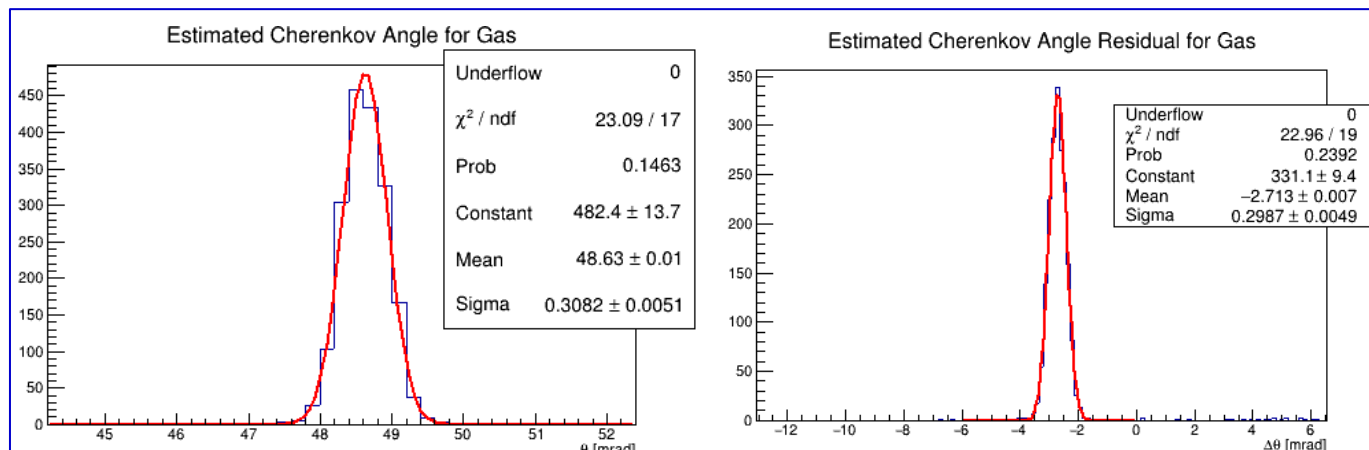
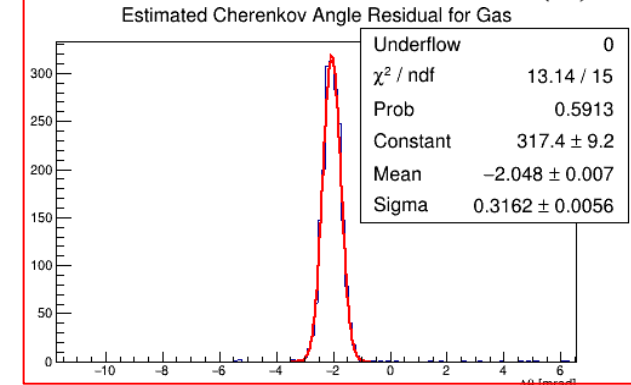
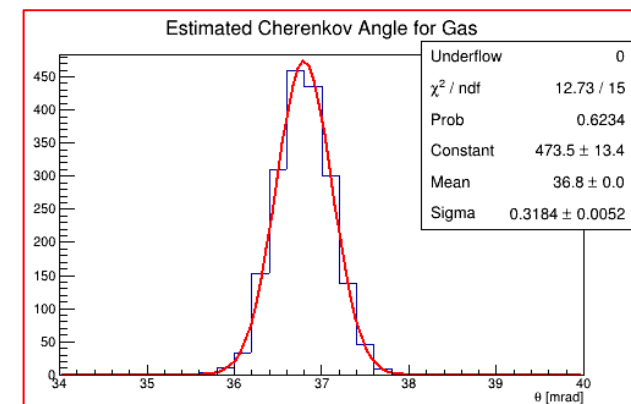
We should consider the option of a pressurized argon radiator and fully prepare this option

Comparison of C4F10 and C2F6 in ePIC simulations

Slide provided by Chandradoy Chatterjee

50 GeV/c pions and kaons shot at eta 2.5

Gas	Npe(pi /K)	Th_pi	Th_K	Sig_pi	Sig_K	N_Sig
C2F6	16.03/ 14.94	36.8	35.67	0.32	0.33	3.5
C4F10	24.8/2 3.8	48.63	47.8	0.29	0.30	2.8



- C4F10 does not qualify the 3.5 sigma test.
- Offset of 2 mrad in theta residual is present consistently in both gases.
- The number of photons compatible to COMPASS for C4F10 (for PMTs we have $\langle N_{pe} \rangle \sim 60$ at saturation)

CONCLUSIONS

- **COMPASS/AMBER and LHCb RICHs successfully running with C_4F_{10}**
 - COMPASS gas system has "large" leaks, which may be not tolerated at EIC
 - New gas systems can have very small leaks (at a price ...)
- **Can C_2F_6 be purchased in sufficient quantity and stored ?**
- **Should a set of possible alternatives: NOVECs, gas mixtures, ... be studied ?**
 - The risk of a total ban of PFAS cannot be excluded
- **Should the pressurized argon option be considered as first choice ?**