# Green use of fluorocarbons in Cherenkov detectors and silicon tracker cooling systems: challenges and opportunities.


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**G. Hallewell: Green FCs for Cherenkov detectors and Si tracker cooling: Sustainability session ICHEP2024 Praque 18-24 July 2024**

# "Green" fluorocarbons for Cherenkov detectors & silicon tracker cooling systems: challenges and opportunities

- ***Saturated fluorocarbons (PFCs, SFCs: $C_nF_{(2n+2)}$)*** chosen for optical properties as Cherenkov radiators: $C_4F_{10}$ & $CF_4$ in COMPASS & LHCb RICH1&2.

- **Non-conductivity, non-flammability, non-toxicity & radiation resistance ➔ ideal coolants**
  - **$C_6F_{14}$ used in all LHC experiments,**
  - **$C_3F_8$ evaporatively cools ATLAS silicon tracker, TOTEM;**

- **These fluids however have high GWPs ($GWP_{20}$ > 5000*$CO_2$);**

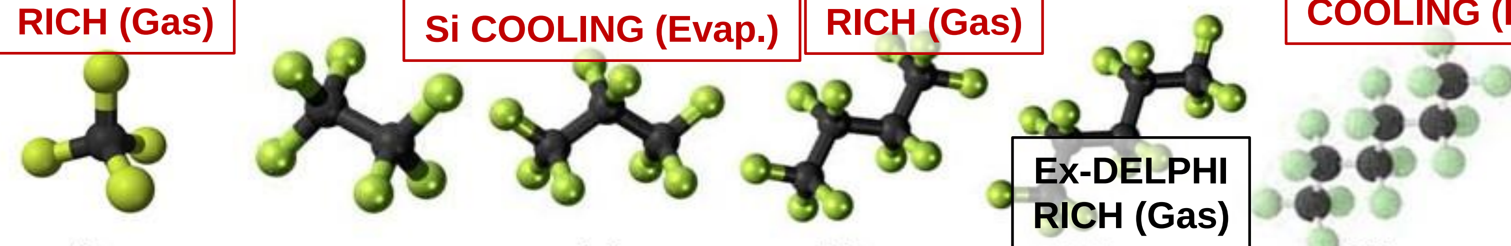
- ***Fluoro-ketones ($C_nF_{2n}O$),*** **while not industrialised over a wide $C_nF_{2n}O$ range, can offer similar performance at very low, or 0 GWP;**

- **Radiation tolerance & thermal performance of 3M NOVEC 649 (lin-$C_6F_{12}O$) sufficiently promising to be considered by CERN to replace $C_6F_{14}$ for cooling;**

# Molecular shapes and GWP (1)

## SATURATED FLUOROCARBONS ($C_nF_{(2n+2)}$) with current uses at CERN

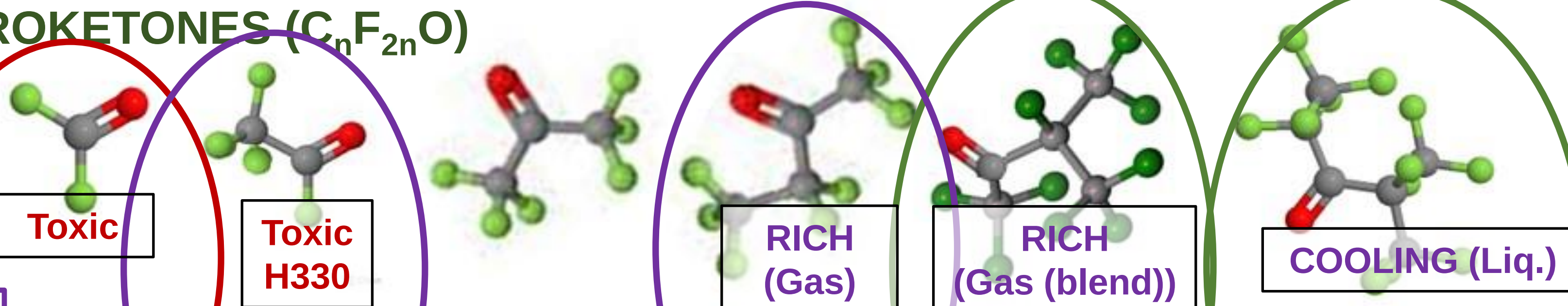
Current uses at CERN




| $CF_4$ | $C_2F_6$ | $C_3F_8$ | $C_4F_{10}$ | $C_5F_{12}$ | $C_6F_{14}$ |
|---|---|---|---|---|---|
| ($GWP_{20}$ = 4880) | ($GWP_{20}$ = 8210) | ($GWP_{20}$ = 6640) | ($GWP_{20}$ = 6870) | ($GWP_{20}$ = 6350) | ($GWP_{20}$ = 5890) |
| [16] | [16] | [16] | [16] | [16] | [16] |

## FLUOROKETONES ($C_nF_{2n}O$)

Probable Uses (if/when available)



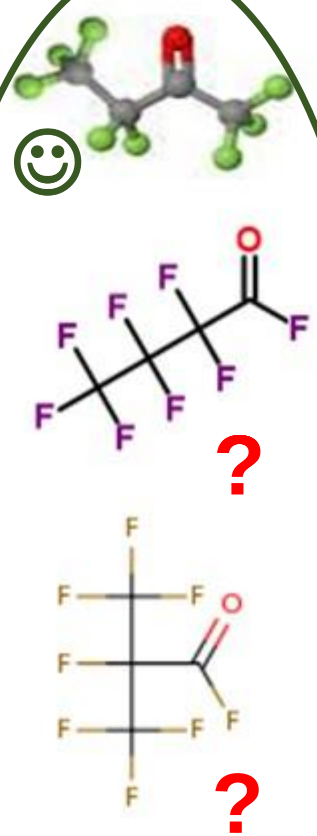

| $CF_2O$ | $C_2F_4O$ | $C_3F_6O$ | $C_4F_8O$ | NOVEC 5110 $C_5F_{10}O$ | NOVEC 649 $C_6F_{12}O$ |
|---|---|---|---|---|---|
| ($GWP_{20}$ = ?) | ($GWP_{20}$ = ?) | ($GWP_{20}$ = ?) | ($GWP_{20}$ = ?) | ($GWP_{20}$ = ≤ 1) | ($GWP_{20}$ = ≤ 1) |
| | $CF_3C(O)F$ | $CF_3C(O)CF_3$ | $CF_3CF_2C(O)CF_3$ | [13] | [12] |
| | | | | $CF_3C(O)CF(CF_3)_2$ | $CF_3CF_2C(O)CF(CF_3)_2$ |

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

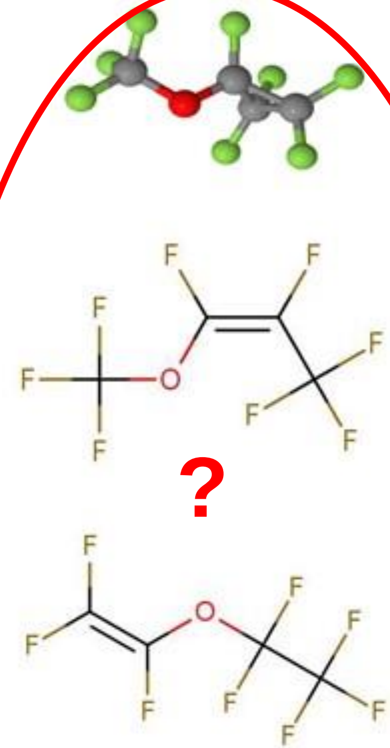
***Lower*: shapes of some non-cyclic $C_nF_{2n}O$ analogues**

**(20-year GWPs noted where known – refs: https://link.springer.com/article/10.1140/epjp/s13360-023-04703-w)**

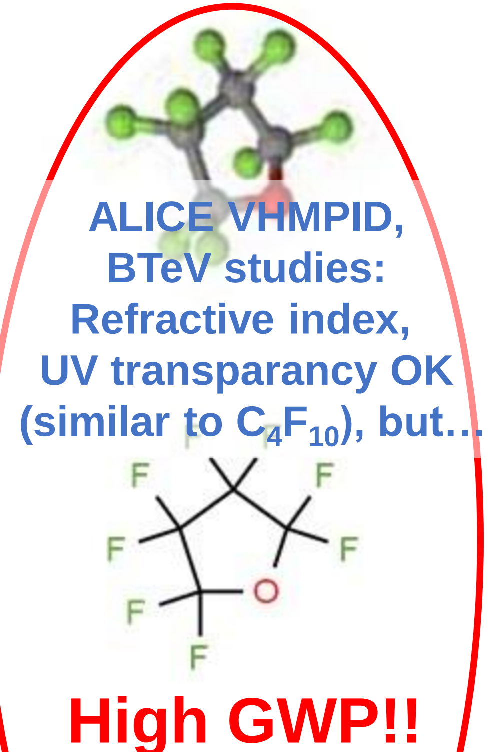
# Molecular shapes and GWP (2)



$C_4F_8O$
Linear & branched with Oxygen atom on external spur
($GWP_{20}$ = ?)



$C_4F_8O$
Linear with Oxygen atom as internal link and double carbon bonded link
($GWP_{20}$ = ?)




$C_4F_8O$
Cyclic
Perfluorotetrahydrofuran,
Octofluorotetrahydrofuran
($GWP_{20}$ = 8975) [10]

**Cyclic, non-cyclic & non-cyclic double carbon-bonded $C_4F_8O$ isomers: refs at end.**

***Placement of oxygen atom can also determine flammability & toxicity***

From: 2021-22 CERN environmental Report report

https://doi.org/10.25325/CERN-Environment-2023-003


| GROUP | GASES | $tCO_2e$ 2021 | $tCO_2e$ 2022 |
|---|---|---|---|
| Perfluorocarbons (PFCs) | $CF_4$, $C_2F_6$, $C_3F_8$, $C_4F_{10}$, $C_6F_{14}$ | 55 921 | 68 989 |
| Hydrochlorofluorocarbons (HFCs) | HFC-23 ($CHF_3$)<br>HFC-32 ($CH_2F_2$)<br>HFC-134a ($C_2H_2F_4$)<br>HFC-404a<br>HFC-407c<br>HFC-410a<br>HFC-507 | 36 557 | 86 211 |
| Other F-gases | $SF_6$, $NF_3$ | 16 838 | 18 355 |
| Hydrofluoroolefins (HFO)/HFCs | R-449<br>R1234ze<br>NOVEC 649 | 86 | 199 |
| | $CO_2$ | 13 771 | 10 419 |
| **Total Scope 1** | | 123 174 | 184 173 |

PFC Loss around 10-12 tonnes (particle detection and detector cooling)

GWP 23000

GWP 0

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# Adding some conclusion here, *in case I run out of time*:

"Green" fluorocarbons for Cherenkov detectors & silicon tracker cooling systems: challenges & opportunities

- **Saturated fluorocarbons (SFCs: $C_nF_{(2n+2)}$) chosen for optical properties as Cherenkov radiators: $C_4F_{10}$ & $CF_4$ used in COMPASS & LHCb RICH1&2.**
- **Non-conductivity, non-flammability & radiation resistance → ideal coolants**
  - **$C_6F_{14}$ used in all LHC experiments,**
  - **$C_3F_8$ evaporatively cools ATLAS silicon tracker, TOTEM.**
- **These fluids however have high GWPs ($GWP_{20}$ > 5000*$CO_2$).**
- **While not industrialised over a wide $C_nF_{2n}O$ range fluoro-ketones can offer similar performance at very low, or 0 GWP;**
- **Radiation tolerance & thermal performance of 3M NOVEC 649 (lin-$C_6F_{12}O$) sufficiently promising to be considered by CERN to replace $C_6F_{14}$ for cooling;**
- ***Cherenkov detectors*: subject to optical testing, *lin-$C_4F_8O$ could replace $C_4F_{10}$* while *lin-$C_4F_8O$ or lin-$C_5F_{10}O$ blended with $N_2$ and monitored in real time by sound velocity gas analysis - could replace $CF_4$* in RICH radiators;**
- ***SI tracker COOLING: Lighter molecules (e.g. $C_2F_4O$, with similar thermodynamics to $C_2F_6$) - would allow lower temperature, 0GWP operation than evaporative $CO_2$ in Si trackers operated at high luminosity: low order $C_nF_{2n}O$ toxicity a problem…***

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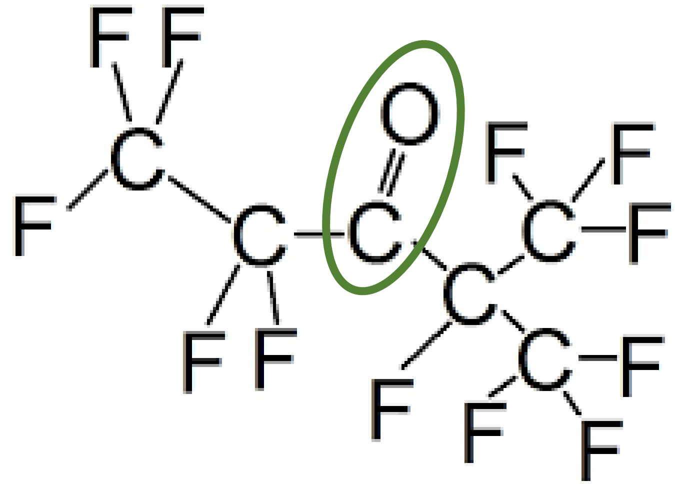
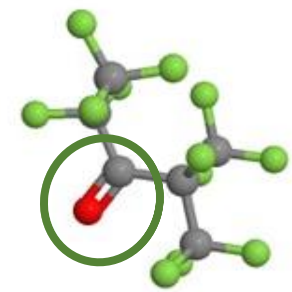
**Sustainability session: ICHEP2024 Prague 18-24 July 2024**

# What gives NOVEC 649/1230 (lin $C_6F_{12}O$: FK-5-1-12) its low GWP?





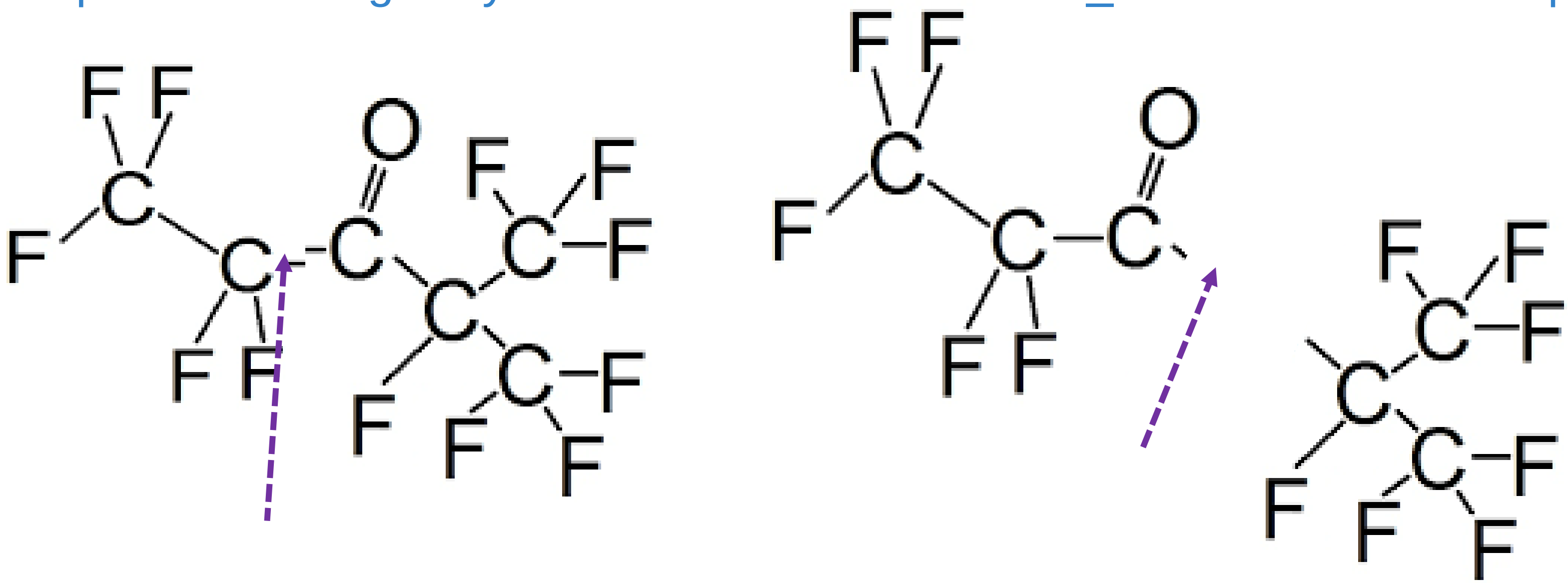
NOVEC 649 $C_6F_{12}O$
($GWP_{20}$ = ≤ 1)
[12]
$CF_3CF_2C(O)CF(CF_3)_2$

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

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

# What gives NOVEC 649/1230 (lin $C_6F_{12}O$: FK-5-1-12) its low GWP?

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

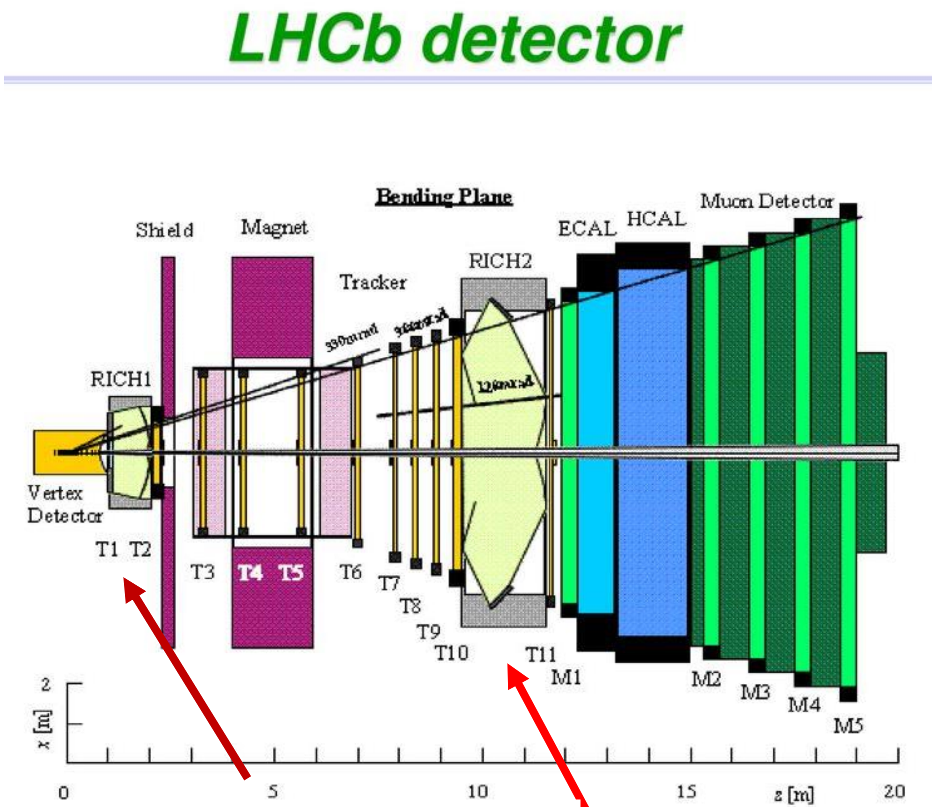


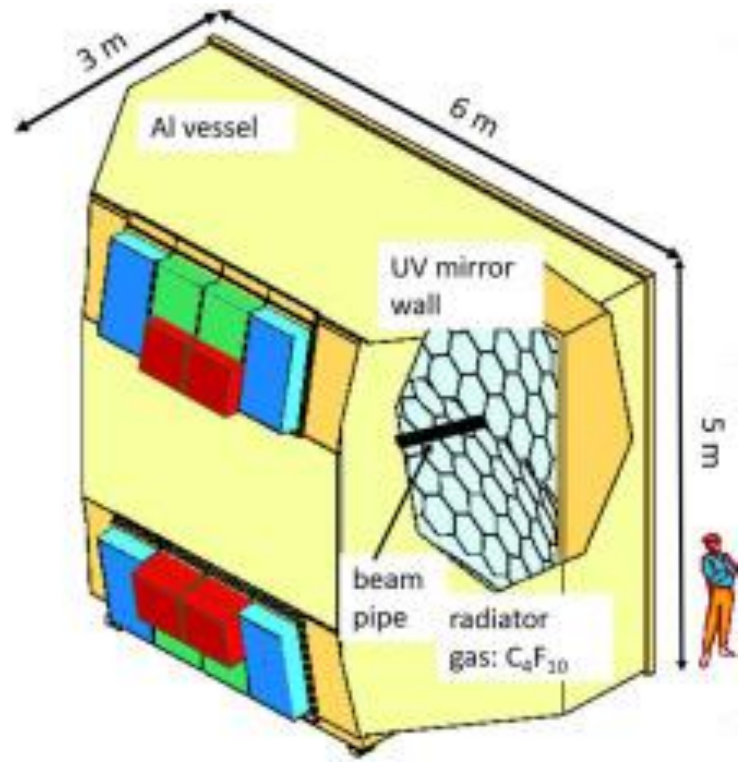
**Scission by UV photons of λ ~300 nm in upper atmosphere (low P, high UV): fragments do not re-associate* into $C_nF_{(2n+2)}$ SFCs**

***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**

# The Cherenkov detector aspect

# Ideally… replace SFCs with same-order $GWP_0$ FKs *with good UV transparency, refractivity…*



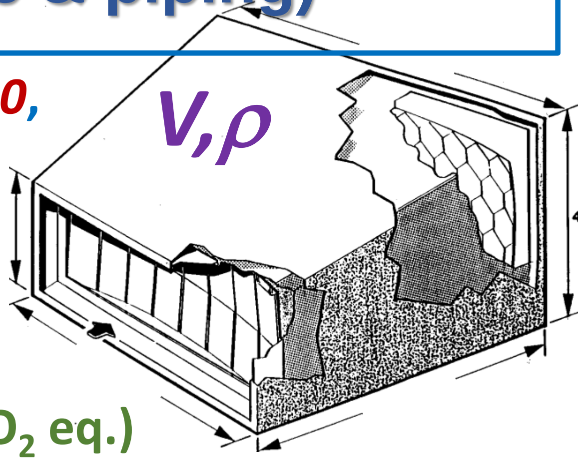

**LHCb RICH 1**
($4m^3$ lin-$C_4F_8O$)
GWP eqv. $CO_2$: 0 tonnes

**LHCb RICH 2**
(100 $m^3$: $CF_2O$ + ?)
**No! $CF_2O$ TOXIC ☹**

**COMPASS RICH**
(100 $m^3$ lin- $C_4F_8O$)
GWP eqv. $CO_2$: 0 tonnes

# Refractive index & GWP 'load' in a Cherenkov Gas Radiator (vessel only, not including tankage & piping)

$C_4F_{10}$ (COMPASS: 100m$^3$, LHCb RICH 1: 4m$^3$): *$GWP_{20}$ = 4880*,
$CF_4$ (LHCb RICH 2: 100m$^3$): *$GWP_{20}$ = 6870*




Cherenkov radiator vessel volume *V(m$^3$)* filled with
a blend of gases of densities *$\rho_i$ (kgm$^{-3}$)*,
fractional concentrations *$w_i$* & individual *$GWP_i$* (tonnes $CO_2$ eq.)
has a GWP environmental "load" (& release potential) *L* given by:

$$L = \frac{V}{1000} \sum_i \left( wi \, . \, \rho_i \, . \, GWPi \right) \quad \text{(tonnes } CO_2 \text{ eq.)}$$

Corresponding radiator gas mixture refractivity given by :

$$(n-1)_{rad} = \sum_i \left( wi . (n-1)_i \right)$$

Can blend small concentration $\omega_x$ of (heavier) SFC or Lin-FK vapour of high refractivity *$(n\text{-}1)_x$* with $\omega_y$ of light transparent gas ($N_2$, Ar… ) to replicate the target refractivity *$(n\text{-}1)_z$* of a lighter SFC at high concentration – for lower GWP load.

$$\omega_x = \frac{(n-1)_{z(target)} - (n-1)_y}{(n-1)_x - (n-1)_y}$$

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## Use real-time speed of sound to get component molar concentrations, $\omega_i$ (SoS traditionally also called "c" by acousticians to confuse things)

$$c = \sqrt{\frac{\gamma RT}{M}} \quad \gamma_m = \frac{C_{pm}}{C_{vm}} = \frac{\sum_i w_i Cp_i}{\sum_i w_i Cv_i} \quad M = \sum_i w_i M_i \quad c = \sqrt{\frac{\frac{\sum_i w_i Cp_i}{\sum_i w_i Cv_i} RT}{\sum_i w_i M_i}}$$

More details (ATLAS system): https://www.mdpi.com/2410-390X/5/1/6

**Then use standard refractivity formula to get from calculated $\omega_{1,2}$**

$$(n-1)_{rad} = \sum_i \left(wi.(n-1)_i\right)$$

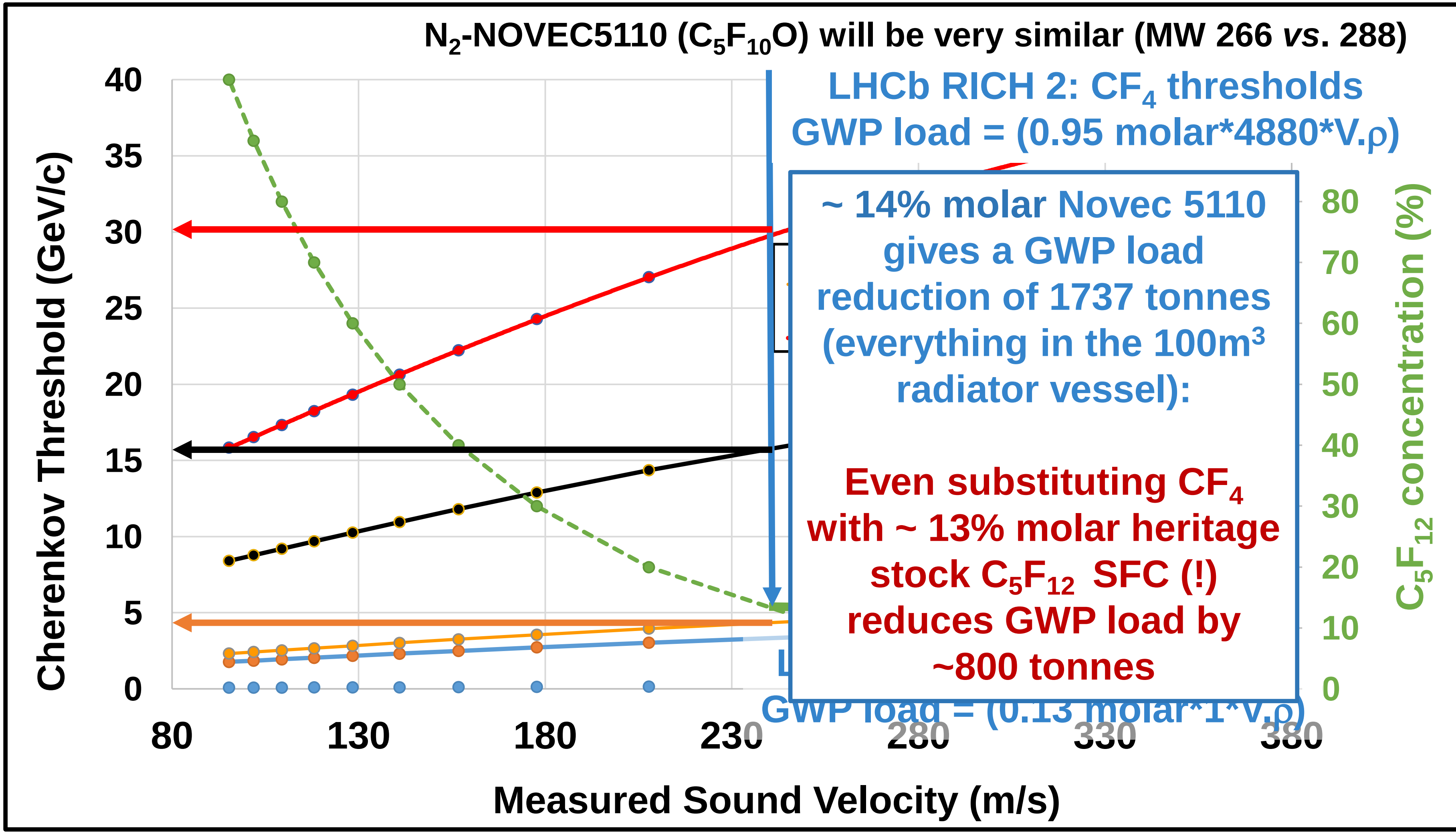
**to refractive index of radiator gas blend in real-time, then standard relativistic expressions to get from n to Cherenkov $\gamma$ thresholds for different particle species + $\beta = 1$ angle**

**Real-time measurement of *speed of sound c* takes us via the relative concentrations of the components to the *speed of light* $\beta$ *and beyond!!* in the radiator gas**

**Eyes on the prize…(focus here on LHCb RICH2 (n-1)…)**
$$(488.10^{-6})_{CF4} = (\sim 1750.10^{-6})_{C5F10O} * 0.12 + (300.10^{-6})_{N2} * 0.88$$

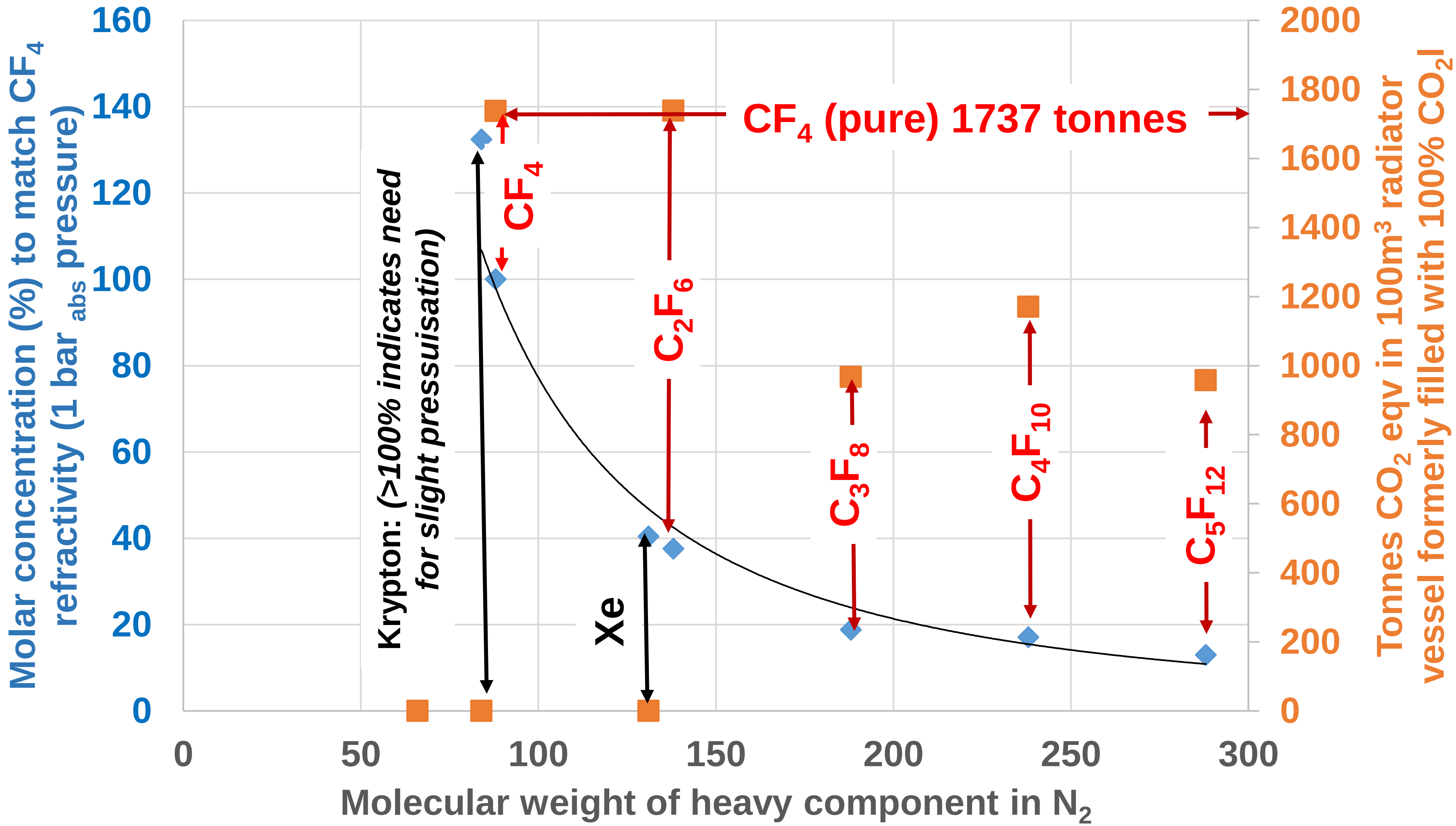
# Cherenkov threshold: *lin*-$C_5F_{10}O$ (eg: 3M NOVEC 5110)/$N_2$ & (heritage) $C_5F_{12}/N_2$ blend

## *and GWP load comparison with LHCb RICH2 ($CF_4$: 100m$^3$)*



# Radiator volume GWP load: 100 m³ gas radiator with different mw gases blended with nitrogen to replace $CF_4$

**(note: blends with Ar very similar: need refractivity data for linear fluoro-ketones, probably similar to SFCs)**
**blends with $CO_2$ not consdered: high $CO_2$ triple point temp (-56 C) ➔ thermodynamic recirculation difficulty)**

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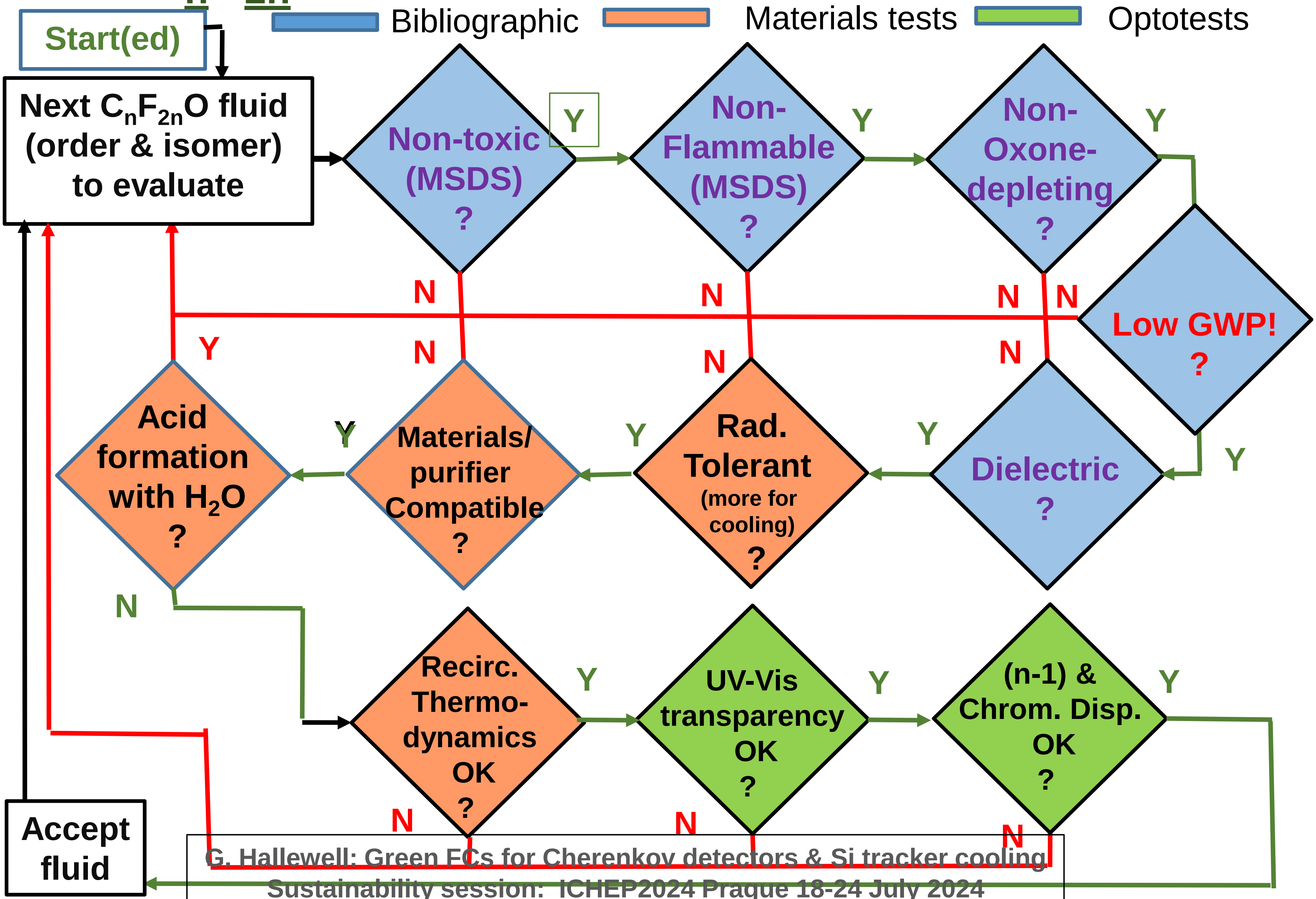
# Even bigger GWP load reduction through $C_4F_{10}$ index matching (eg here: COMPASS RICH)

**Table 1**: GWP loads of various SFCs and NOVEC 5110 blended with $N_2$ ((n-1) = $310.10^{-6}$) to match refractivity of $CF_4$ and $C_4F_{10}$ assumed radiator volume: 100 $m^3$

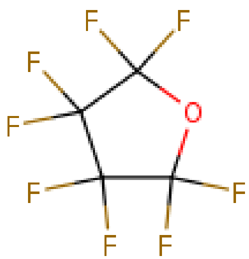
| Base fluid | Base fluid density (1bar,25˚C) $kgm^{-3}$ | Base fluid GWP (20-yr) | Component (n-1) ($*10^6$) (@ nm) | % Blend with $N_2$ to match (n-1) $CF_4$ | GWP load ($t.CO_2$) | % Blend with $N_2$ to match (n-1) $C_4F_{10}$ | GWP load ($t.CO_2$) |
|---|---|---|---|---|---|---|---|
| $CF_4$ LHCb RICH2 (100$m^3$) | **3.56 [18]** | **4880 [16]** | **488 (180-310 nm) [19]** | **100** | **1737** | **not applicable** | **n/a** |
| *$CF_2O$* | - | | | *~100* | *0* | n/a | n/a |
| $C_2F_6$ | 5.63 [18] | 8210 [16] | 793 (180-310 nm) [19] | 38.1 | 1762 | not applicable | n/a |
| *Lin-$C_2F_4O$* | - | | | - | | n/a | n/a |
| $C_3F_8$ | 7.75 [18] | 6640 [16] | 1180 (250 nm) [16] | 21.4 | 1099 | not applicable | n/a |
| *Lin-$C_3F_6O$* | - | | | - | | n/a | n/a |
| $C_4F_{10}$ LHCb RICH1 (4$m^3$): COMPASS (100$m^3$) | **9.97 [18]** | **6870 [16]** | **1450 (250 nm) [16]** | **16.3** | **1119** | **100** | **6849** |
| *Lin-$C_4F_8O$ (Non-cyclic $C_4F_8O$)** | *9.5 (est.)* | *Probably < 1 (NOVEC 5110 Analogy)* | *1380 @ 400nm (based on 3M PFG-3480 c-$C_4F_8O$ [7]: linear $C_4F_8O$ not yet measured but assumed similar)* | *18.4* | *0.18* | *112.7* (>100% would imply necessity of operating $C_4F_8O$ at slight overpressure)* | *1.07* |
| $C_5F_{12}$ | 11.63 [18] (BP 30 ˚C at 1 bar) | 6350 [16] | 1750 (180-310nm)[19] (40 ˚C, undiluted) | 13.0 | 957 | 79.3 | 5857 |
| NOVEC 5110 $C_5F_{10}O$ | 10.7 [13] (BP 27 ˚C at 1 bar) | <1 [13] | Not yet measured: probably around 1650 by analogy with $C_4F_{10}$ and $C_4F_8O$ ratio | 13.9 | 0.149 | 85.2 | 0.91 |

# $C_nF_{2n}O$ fluid selection search criteria



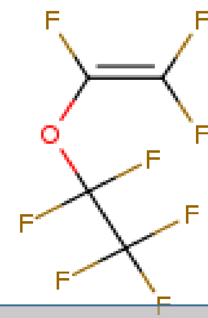
# Some molecular shapes to study (or eliminate) for UVT, GWP, radiation stability & materials compatibility: example: $C_4F_8O$ isomers,

Octafluorotetrahydrofuran
**CAS:** 773-14-8
H332 asphyxiant hazard

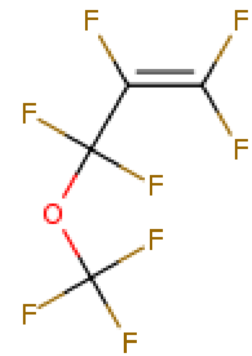


**BTeV, ALICE VHMPID evaluated; good properties but high GWP**

Pentafluoroethyl trifluorovinyl ether
**CAS: 10493-43-3**
Flammable,
H332 Inhalation toxicity Cat 4

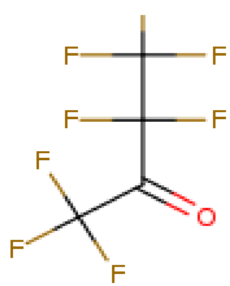


Octafluoro-3-methoxyprop-1-ene
**CAS:** 67641-44-5
H332 Inhalation toxicity Cat. 4

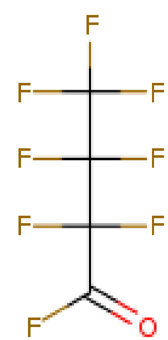


Source: https://www.synquestlabs.com

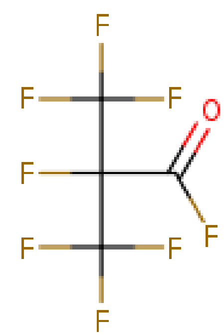
**Octafluoro-2-butanone**
**CAS**: 337-20-2
**Most promising candidate? analogy with NOVEC 5110, 649 structures…**



2,2,3,3,4,4,4-Heptafluorobutanoyl Fluoride **CAS**: 335-42-2
H331 Inhalation toxicity Cat. 3



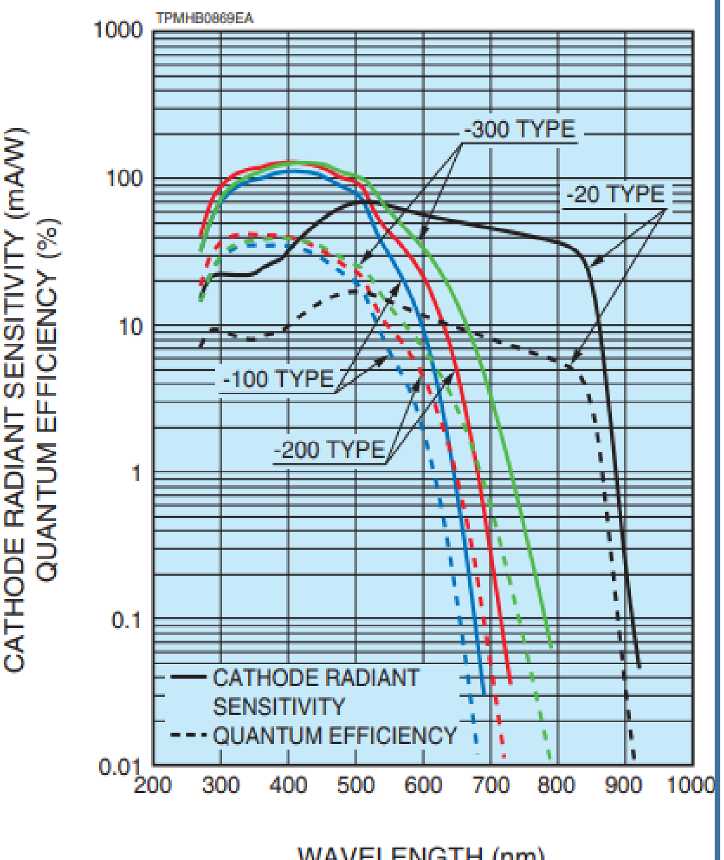
Heptafluoroisobutyryl Fluoride **CAS**: 677-84-9
H331 Inhalation toxicity Cat. 3



# UV transparency, refractivity, cmhemical stability & compatibility studies needed for different $C_nF_{2n}O$ molecular shapes.

## RICH detector community very competent & equipped for detailed UVT & (n-1)

Figure 1: Typical spectral response




**Most probable PC spectral range in new build gas RICH detectors**

*T.V. Acconcia et al. / Nuclear Instruments and Methods in Physics Research A 767 (2014) 50–60*

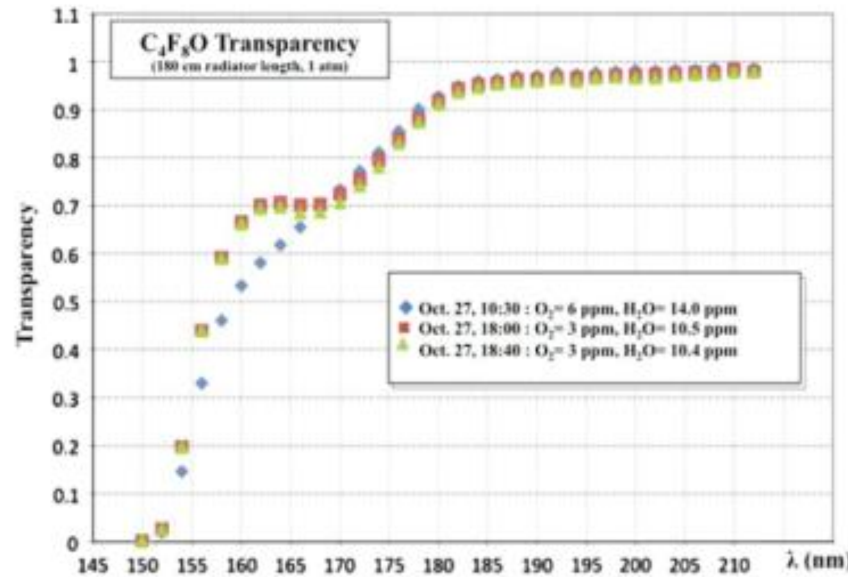


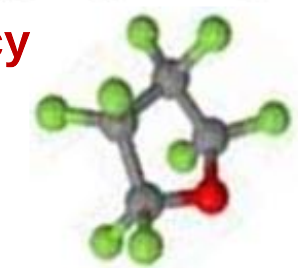

**Fig. 24.** Three transparency measurements of the radiator gas during the same day.

**ALICE VHMPID: transparancy measurements in c-$C_4F_8O$**

Octafluorotetrahydrofuran

CAS: 773-14-8

Synquest Inc. FL, USA



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# On the turning away…

## The uncertain ECHA (European Chemicals Agency) route to fluorocarbon (PFC, PFAS…) prohibition

*(Other people here will talk about this...Path paved with impracticalities?)*

[51] ECHA/NR/23/04;
https://echa.europa.eu/-/echa-publishes-pfas-restriction-proposal]
[52] ECHA Candidate List of substances of very high concern for Authorisation;
https://echa.europa.eu/candidate-list-table
[53] Annex to the Annex XV restriction report proposal for restriction: Per- & polyfluoroalkyl substances (PFASs); ECHA; 22/03/2023
https://echa.europa.eu/documents/10162/d2f7fce1-b089-c4fd-1101-2601f53a07d1
[54] Per- and polyfluoroalkyl substances (PFAS); ECHA
https://echa.europa.eu/hot-topics/perfluoroalkyl-chemicals-pfas

Au revoir 3M… need to clarify manufacturers' attitudes (Dehon Co. (Fr), Synquest (USA), F2 (UK), various companies in China)…
on future *lin*-fluoroketone ($C_nF_{2n}O$) production
Electronics industry is the driver: we just ride the coat-tails!

# The Silicon tracker cooling aspect

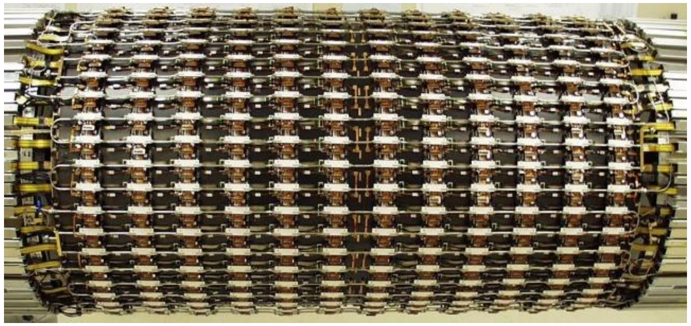
# See also

https://link.springer.com/article/10.1140/epjp/s13360-023-04703-w

# Examples from cooling particle physics Si trackers (ATLAS, CMS, LHCb)

## *Two distinct types of detector cooling geometry at HL-LHC:*

## *(1) Tube and block 'DNA'*



ATLAS barrel SCT (present)

***Thermal Figure of Merit (TFM):***

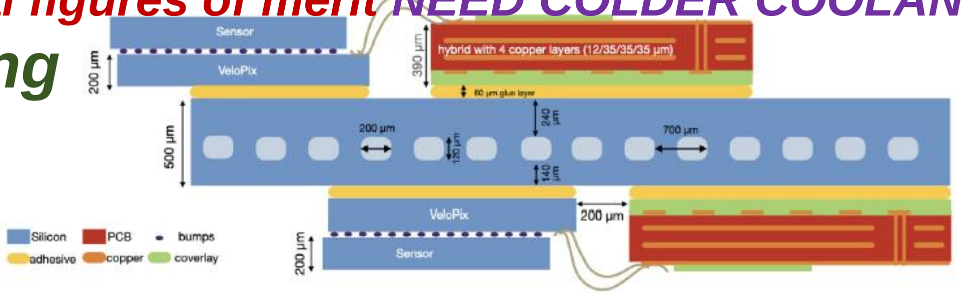
Expressed in terms of temperature difference between Si modules & coolant at given power density (units: °C cm$^2$ W$^{-1}$)

**TFM = (($T_{(\text{Si module})}$ − $T_{(\text{Coolant})}$) / (Si module power/cm$^2$)).**

Lower numeric value ➔ better thermal performance.
TFMs < 4 typical in microchannel devices,
~ 20+ in some tube & block geometries.

***Disadvantages: long(er) heat conduction path (more interfaces) Si ➔ cold(er) coolant: lower Thermal figures of merit NEED COLDER COOLANT!***

## *(2) Micro-channel cooling*




LHCb VELO upgrade

***Advantages: shortest heat conduction path to coolant: coolant can be warmer:***

***Disadvantages: fraglity issues: channels etched in silicon and cover plate attached***

# *Micro-channel cooling: the LHCb VELO upgrade*

## Recent mastery of evaporative $CO_2$ cooling in microchannels

# $CO_2$ Evaportive cooling problems:

***High triple point temperature of -56 °C***

***limits the lowest temperature attainable in the tubes of a tube & block cooling system: $CO_2$ cooling now admitted to be insufficient for protection against radiation damage and protection against leakage current-generated thermal runaway over the whole HL-LHC envelope (2029-41):***

see: L. Contiero et al; Cold Krypton system for the Phase III Upgrade of the LHC, Forum on Tracking Detector Mechanics 2023, Tuebingen Germany May 31-June 2 2023

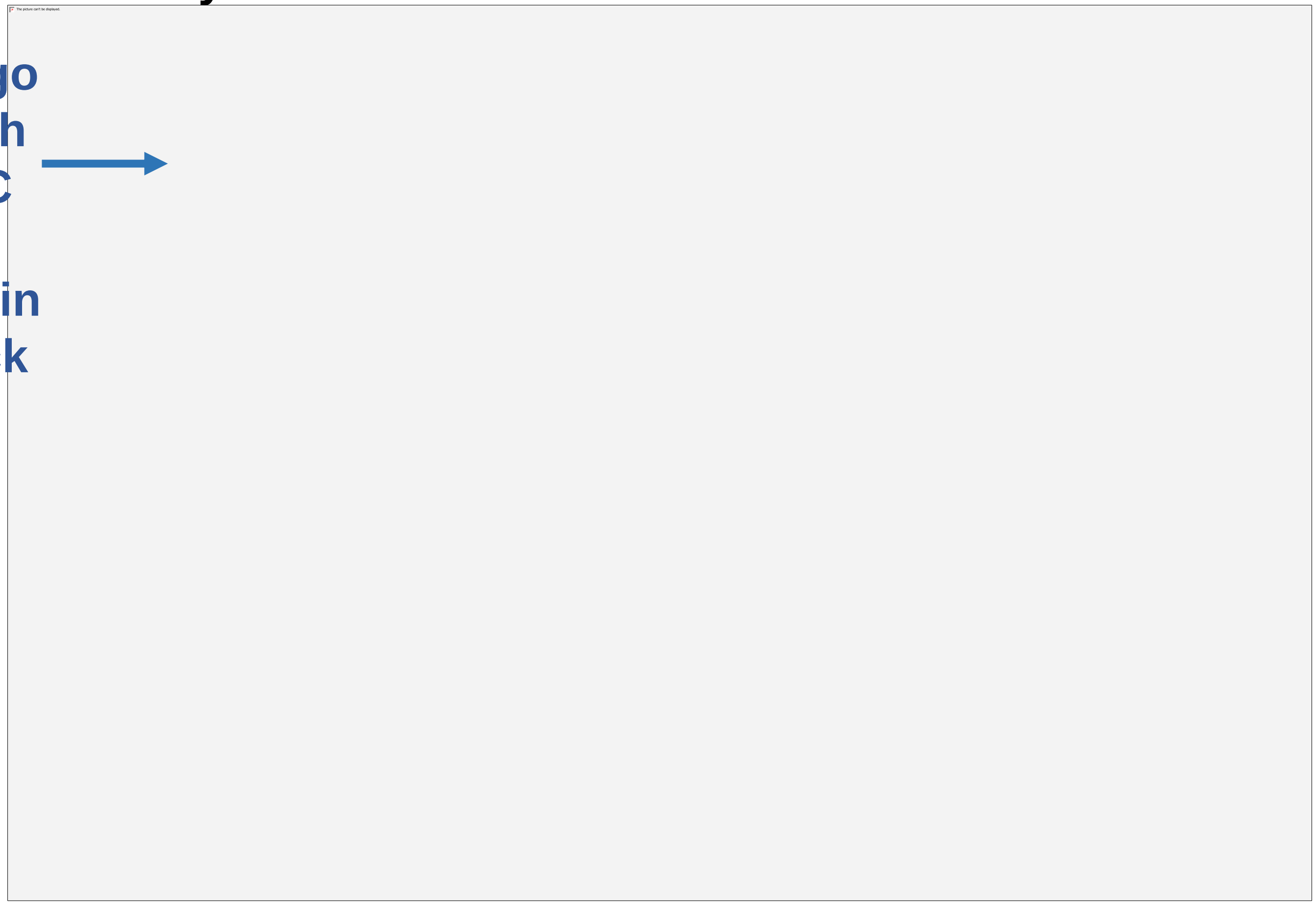
***ATLAS plans to change its inner pixel detector half way through…***

***$CO_2$ cooling already known to be inefficient at coolant temperatures below -40 °C:***

***A very complicated trans-critical krypton evaporative cycle has been proposed***

# Si tracker evaporative coolingome Thermodynamic comparisons: SFCs, $CO_2$, Xe
## (F-K thermodynamics would be similar to same carbon order SFCs)

$C_3F_8$ won't go cold enough for HL-LHC operation, particularly in tube & block trackers



https://link.springer.com/article/10.1140/epjp/s13360-023-04703-w

$C_2F_4O$ would have been the ideal fluid: much cheaper than Xe, but toxic…
blend $C_2F_6$ with $C_3F_6O$?? ($C_2F_6$ / $C_3F_8$ zeotropic blends already demonstrated…)
R. Bates et al; 2015 JINST 10 P03027

# On the turning away…

## The uncertain ECHA (European Chemicals Agency) route to fluorocarbon (PFC, PFAS…) prohibition

*(Other people here will talk about this...Path paved with impracticalities?)*


[51] ECHA/NR/23/04;
https://echa.europa.eu/-/echa-publishes-pfas-restriction-proposal]
[52] ECHA Candidate List of substances of very high concern for Authorisation;
https://echa.europa.eu/candidate-list-table
[53] Annex to the Annex XV restriction report proposal for restriction: Per- & polyfluoroalkyl substances (PFASs); ECHA; 22/03/2023
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[54] Per- and polyfluoroalkyl substances (PFAS); ECHA
https://echa.europa.eu/hot-topics/perfluoroalkyl-chemicals-pfas


Au revoir 3M… need to clarify manufacturers' attitudes (Dehon Co. (Fr), Synquest (USA), F2 (UK), various companies in China)… on future *lin*-fluoroketone ($C_nF_{2n}O$) production

Electronics industry is the driver: we just ride the coat-tails!

# Conclusion
# (See the beginning as I didn't think I'd get this far…)

Anyway… thanks for watching and listening:

(some references and back-up material follow
for those interested in this subject)

Also see: https://link.springer.com/article/10.1140/epjp/s13360-023-04703-w

# Well, if you insist…

- **Saturated fluorocarbons (SFCs: $C_nF_{(2n+2)}$) are chosen for their optical properties as Cherenkov radiators, with $C_4F_{10}$ and $CF_4$ used in COMPASS & LHCb RICH1&2.**
- **Non-conductivity, non-flammability & radiation resistance ➔ ideal coolants with $C_6F_{14}$ used in all LHC experiments, while $C_3F_8$ evaporatively cools the ATLAS silicon tracker and TOTEM.**
- **These fluids however have high GWPs ($GWP_{20}$ > 5000*$CO_2$).**
- **While not industrialised over a wide $C_nF_{2n}O$ range fluoro-ketones can offer similar performance at very low, or 0 GWP;**
- **Radiation tolerance & thermal performance of 3M NOVEC 649 (lin-$C_6F_{12}O$) sufficiently promising to be considered by CERN to replace $C_6F_{14}$ for cooling;**
- **Subject to optical testing, *lin-$C_4F_8O$ could replace $C_4F_{10}$* while *lin-$C_4F_8O$ or lin-$C_5F_{10}O$ blended with $N_2$ and monitored in real time by sound velocity gas analysis - could replace $CF_4$* in RICH detectors;**
- ***Lighter molecules (e.g. $C_2F_4O$, with similar thermodynamics to $C_2F_6$) - would allow lower temperature, 0GWP operation than evaporative $CO_2$ in Si trackers operated at high luminosity, but low order $C_nF_{2n}O$ toxicity a problem…***

# References and back-up material

## Approaches to low-GWP fluorocarbon RICH radiator gases

.

**See also:**

(1) https://link.springer.com/article/10.1140/epjp/s13360-023-04703-w
(paper: EuroPhysics J. Plus, Dec 2023)

(2) https://indico.cern.ch/event/1263731/contributions/5398511/attachments/2648319/4584649/G_Hallewell_DRD4%20Rad%20Gas%20GWP%20with%20annexes%20May%2016%202023.pdf

(3) https://indico.cern.ch/event/1410802/ (DRD4 WG2 meeting 17 May 2024)

(4) https://indico.cern.ch/event/1420840/ (DRD4 WP_3.1 meeting 28 May 2024)

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[8] **Product** #2H07-2-08 **Synonyms:** 2,2,3,3,4,4,5,5-octafluorotetrahydrofuran, Perfluorotetrahydrofuran**; CAS No:** 773-14-8**, MDL No.** MFCD00465561: SynQuest Labs Inc., 13201 Rachael Boulevard, Alachua, FL 32615, USA https://www.synquestlabs.com/Home/ProductDetail?SearchText=Octafluorotetrahydrofuran
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Options for alternate radiators in LHCb-RICH system (including calculations by O. Ullaland); S. Easo,
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[54] Per- and polyfluoroalkyl substances (PFAS); ECHA https://echa.europa.eu/hot-topics/perfluoroalkyl-chemicals-pfas

# (5.7) SWOT analysis of cooling fluids HL-LHC

## Strengths $CO_2$
Non-flammable, non-toxic, electrical insulator, non-ozone-depleting, radiation resistant, GWP=1

## Weaknesses $CO_2$
High pressure circulation (60 bar) at ambient temp before cooldown to operating temp
High triple point ( -56°C)

## Threats $CO_2$
High triple point may make Si tracker operation problematic: less thermal 'headroom' after heavy irradiaton ('thermal runaway' phenomenon)

## Opportunities $CO_2$
Extensive R&D program at CERN
Evaporative coolant of choice for ATLAS, CMS for start of HL-LHC program

## Strengths xenon
Non-flammable, non-toxic, electrical insulator, non-ozone-depleting, radiation resistant, GWP=0

## Weaknesses xenon
High pressure circulation (50 bar) at ambient temp before cooldown to operating temp (amost transcritical)
Extremely expensive

## Threats xenon
Very difficult future procurement (war in Ukraine) ($10^{-8}$ atmospheric content.)

## Opportunities xenon
Could find expertise In particle physics community for fabrication of circulators: already used in dark matter experiments

## Strengths $C_2F_6$
Non-flammable, non-toxic, electrical insulator, non-ozone-depleting, radiation resistant

## Weaknesses $C_2F_6$
Very high GWP (around 6000 x $CO_2$)

## Threats $C_2F_6$
Production will be phased out unless a strong motivation from semiconductor manufacture industry

## Opportunities $C_2F_6$
Proved to decrease the operating temp of an ATLAS SCT thermal model in blend with 75% $C_3F_8$

## Strengths $C_nF_{2n}O$
Non-flammable, non-toxic, electrical insulator, non-ozone-depleting, radiation resistant, GWP=0

## Weaknesses $C_nF_{2n}O$

## Threats $C_nF_{2n}O$
Large scale industrial production may depend on the phasing-out of SFCs, needs of semiconductor manufacture industry: Material compatibility needs further study.

## Opportunities $C_nF_{2n}O$
Expertise in particle physics community for 3M NOVEC 649 ($C_6F_{12}O$)

# The uncertain ECHA path to prohibition

# (a path paved with impracticalities?)

https://echa.europa.eu/-/echa-publishes-pfas-restriction-proposal

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# All news

## ECHA publishes PFAS restriction proposal

ECHA/NR/23/04

**The details of the proposed restriction of around 10 000 per- and polyfluoroalkyl substances (PFASs) are now available on ECHA's website. ECHA's scientific committees will now start evaluating the proposal in terms of the risks to people and the environment, and the impacts on society.**

**Helsinki, 7 February 2023** – The proposal was prepared by authorities in Denmark, Germany, the Netherlands, Norway and Sweden and submitted to ECHA on 13 January 2023. It aims to reduce PFAS emissions into the environment and make products and processes safer for people.

All PFASs in the scope of the proposal are very persistent in the environment. If their releases are not minimised, people, plants and animals will be increasingly exposed, and without a restriction, such levels will be reached that have negative effects on people's health and the environment. The authorities estimate that around 4.4 million tonnes of PFASs would end up in the environment over the next 30 years unless action is taken.

*Peter van der Zandt*, ECHA's Director for Risk Assessment said: "This landmark proposal by the five authorities supports the ambitions of the EU's Chemicals Strategy and the Zero Pollution action plan. Now, our scientific committees will start their evaluation and opinion forming. While the evaluation of such a broad proposal with thousands of substances, and many uses, will be challenging, we are ready."

**Next steps**

ECHA's scientific committees for Risk Assessment (RAC) and for Socio-Economic Analysis (SEAC) will check that the proposal meets the legal requirements of REACH in their meetings in March 2023. If it does, the committees will begin their scientific evaluation of the proposal. A six-month consultation is planned to start on 22 March 2023.

RAC will form an opinion on whether the proposed restriction is appropriate in reducing the risks to people's health and the environment, while SEAC's opinion will be on the socio-economic impacts, i.e. benefits and costs to society, associated with the proposal. Both committees form their opinions based on the information in the restriction proposal and the comments received during consultations. The committees also consider advice from the Enforcement Forum on the enforceability of the proposed restriction. Once the opinions are adopted, they will be sent to the European Commission who, together with the EU Member States, will then decide on the potential restriction.

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LEGISLATION CONSULTATIONS INFORMATION ON CHEMICALS SUPPORT

ECHA > Information on Chemicals > Candidate List

# Candidate List of substances of very high concern for Authorisation

(published in accordance with Article 59(10) of the REACH Regulation)

**Notes:**

- **Authentic version:** Only the Candidate List published on this website is deemed authentic. Companies may have immediate legal obligations following the inclusion of a substance in the Candidate List on this website including in particular Articles 7, 31 and 33 of the REACH Regulation.
- ***Numerical identifiers***: Each candidate list entry covers both anhydrous and hydrated forms of a substance. The CAS number shown in an entry is typically for the anhydrous form. Hydrated forms of the substance identified by other CAS numbers are still within the scope of the entry.
- ***Other numerical identifiers***: For those entries with "-" in the EC number and CAS number columns, a non-exhaustive inventory of EC and/or CAS Registry numbers describing substances or groups of substances considered to fall within the scope of the Candidate List entry is included, where practicably possible. This information can be accessed through the "Details" button of the selected entry.

**FURTHER INFORMATION**

- More information about Candidate list of Substances of Very High Concern for Authorisation
- Data on Candidate List substances in articles
- Reason for inclusion
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**Annex to the**
**ANNEX XV RESTRICTION REPORT**

**PROPOSAL FOR A RESTRICTION**

**SUBSTANCE NAME(S):** Per- and polyfluoroalkyl substances (PFASs)

**IUPAC NAME(S):** n.a.

**EC NUMBER(S):** n.a.

**CAS NUMBER(S):** n.a.

**CONTACT DETAILS OF THE DOSSIER SUBMITTERS:**


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- Bisphenols
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- Alternatives to animal testing
- Phthalates
- Biocides
- Lead
- Research to enhance protection of our health and environment

# Per- and polyfluoroalkyl substances (PFAS)

Per- and polyfluoroalkyl substances (PFAS) are a large class of thousands of synthetic chemicals that are used throughout society. However, they are increasingly detected as environmental pollutants and some are linked to negative effects on human health.

They all contain carbon-fluorine bonds, which are one of the strongest chemical bonds in organic chemistry. This means that they resist degradation when used and also in the environment. Most PFAS are also easily transported in the environment covering long distances away from the source of their release.

PFAS have been frequently observed to contaminate groundwater, surface water and soil. Cleaning up polluted sites is technically difficult and costly. If releases continue, they will continue to accumulate in the environment, drinking water and food.

Latest updates

Universal PFAS restriction proposal:

- Committees for Risk Assessment and for Socio-Economic Analysis meet in June - stakeholder registration open until 9 May 2024
- Dossier Submitter's ongoing role in the PFAS restriction proposal - news from German BAuA, 15 April 2024
- Next steps for PFAS restriction proposal, 13 March 2024
- Highlights from November RAC and SEAC meetings, 7 Dec 2023
- Enforcement Forum's advice on enforceability of the proposed PFAS restriction, 8 Nov 2023
- All comments submitted to the PFAS restriction proposal now online, 2 Nov 2023

Restriction proposal on PFAS in firefighting foams:

- ECHA's committees: EU-wide PFAS ban in firefighting foams warranted, 22 June 2023

Other:

- Member States vote to restrict PFHxA in the EU, 29 February 2024
- Perfluoroheptanoic acid (PFHpA) and its salts added to Candidate List of substances of very high concern, 17 January 2023

› What are PFAS and what are they used for?

› What are the concerns?

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- Persistent Organic Pollutants (POPs)
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- Community Rolling Action Plan
- Harmonised classification and labelling
- Addressing substances of concern

European Commission and EU institutions

- European Green Deal: Commission proposes rules for cleaner air and water, 26 Oct 2022
- Council formally adopts further restrictions to 'forever chemicals' in waste, 24 Oct 2022
- Chemicals Strategy for Sustainability
- Commission staff working document: Poly- and perfluoroalkyl substances (PFAS)
- EFSA's PFAS draft opinion explained
- Commission welcomes provisional agreement to improve the quality of drinking water and the access to it
- Chemical pollutants —