

## The “green” use of fluorocarbons in Cherenkov detectors challenges and opportunities in an unfolding era of alternatives.

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

### See also:

[https://indico.cern.ch/event/1263731/contributions/5398511/attachments/2648319/4584649/G\\_Hallewell\\_DRD4%20Rad%20Gas%20GWP%20with%20annexes%20May%2016%202023.pdf](https://indico.cern.ch/event/1263731/contributions/5398511/attachments/2648319/4584649/G_Hallewell_DRD4%20Rad%20Gas%20GWP%20with%20annexes%20May%2016%202023.pdf)

[https://indico.cern.ch/event/1371158/contributions/5773321/attachments/2788215/4861759/G\\_Hallewell\\_ATLAS\\_sustainability\\_forum\\_Jan\\_26\\_2024\\_v2.pptx](https://indico.cern.ch/event/1371158/contributions/5773321/attachments/2788215/4861759/G_Hallewell_ATLAS_sustainability_forum_Jan_26_2024_v2.pptx)

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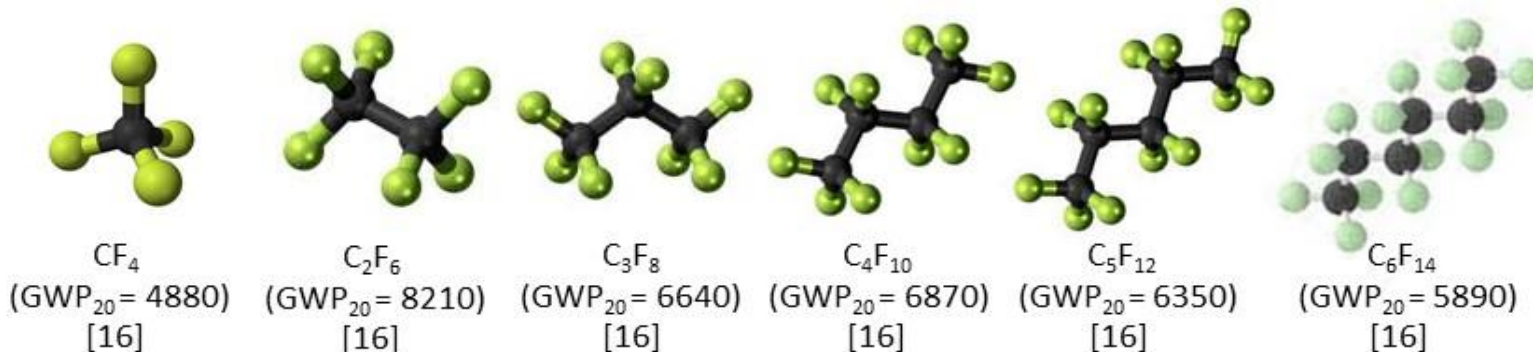
**With thanks to many people for information, as detailed in link (1) above**

# Main points being considered here

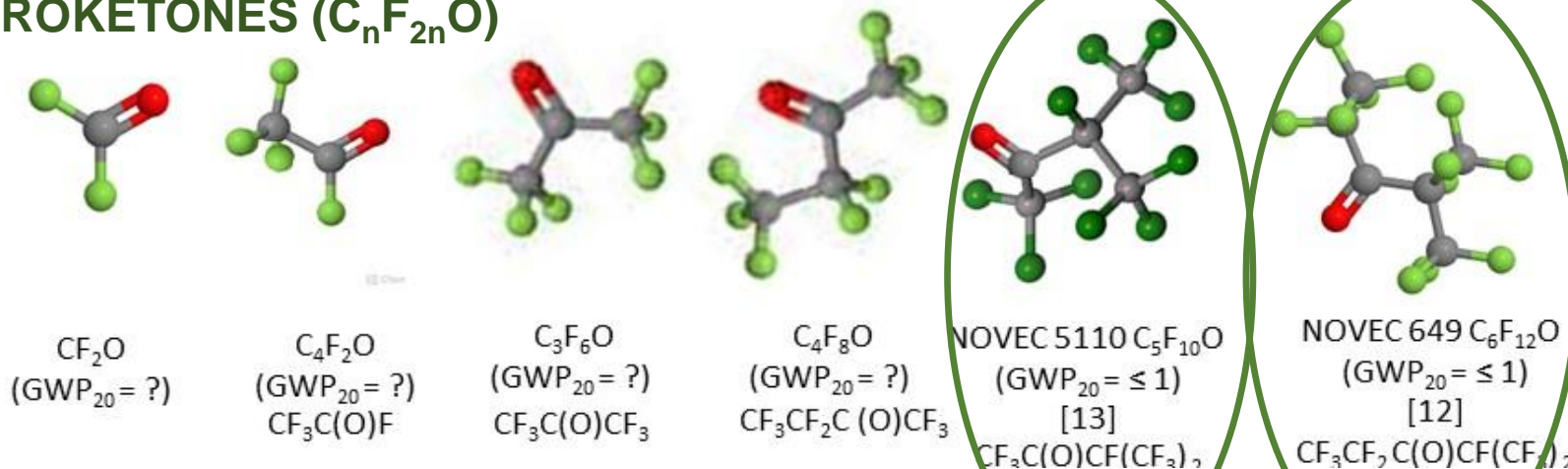
- COMPASS and LHCb use  $C_4F_{10}$  and  $CF_4$  Cherenkov gas radiators. These Saturated FluoroCarbons ( $C_nF_{(2n+2)}$ ) have high GWPs, however (5000-9000\* $CO_2$ ) so there is impetus to reduce their consumption.
- Oxygenated fluorocarbons ( $C_nF_{2n}O$ ) offer similar optical performance, with GWPs equivalent to  $CO_2$ . GWPs are geometry-specific however: closed molecular rings with internal oxygen atom link have GWPs as high as SFCs: *to be avoided*.
- Legislation & market forces will limit FC availability, maybe leaving “holes” in the  $C_nF_x$  “spectrum”, unfilled by  $C_nF_{2n}O$  equivalents.
- Blending low molar concentrations of heritage-stock higher-order SFCs or 3M NOVEC<sup>®</sup>5110:  $C_5F_{10}O$  (GWPzero) with light gases,  $N_2$ , Ar,  $CO_2$ ... would reduce radiator volume GWP “load”.
- Sound velocity monitoring was used for controlling real-time blending  $C_5F_{12}$  with  $N_2$  in the SLD CRID and is used in ATLAS. New algorithms permit use in gas mixtures with known levels of multiple other contaminant gases
- The technique could be valuable in the future operation to meet optical & low GWP constraints of future blended Cherenkov gas radiators.  
*Examples are explored.*

# Molecular shapes and GWP (1)

## SATURATED FLUOROCARBONS ( $C_nF_{(2n+2)}$ )



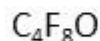
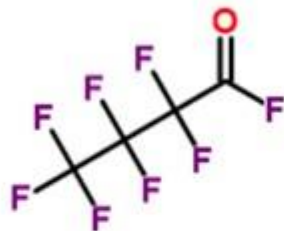
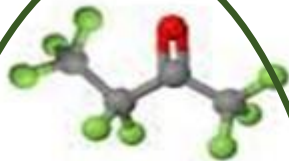
## FLUOROKETONES ( $C_nF_{2n}O$ )



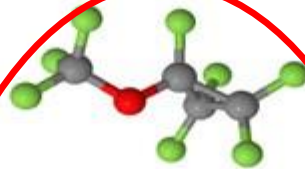
*Upper:* molecular shapes of SFCs, including common gaseous Cherenkov radiators

*Lower:* shapes of some non-cyclic  $C_nF_{2n}O$  analogues  
(20-year GWPs noted where known – refs at end)

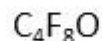
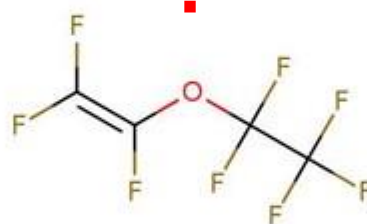
# Molecular shapes and GWP (2)



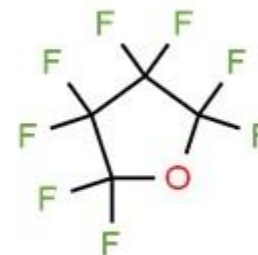
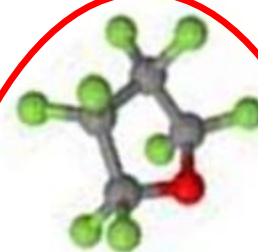
Linear & branched with Oxygen atom on external spur  
(GWP<sub>20</sub> = ?)



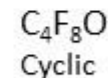
?



Linear with Oxygen atom as internal link  
and double carbon bonded link  
(GWP<sub>20</sub> = ?)



!!



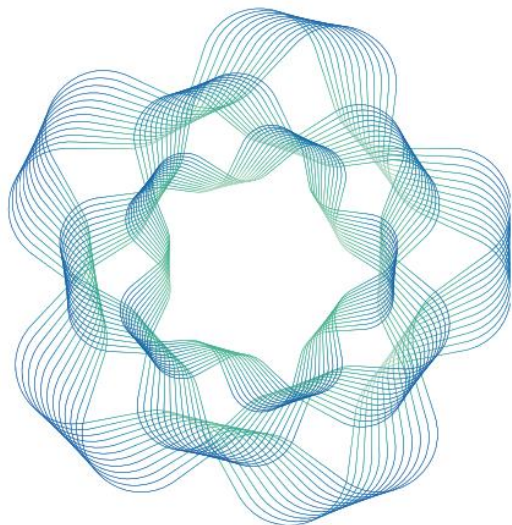
Perfluorotetrahydrofuran  
Octafluorotetrahydrofuran  
(GWP<sub>20</sub> = 8975) [10]

Shape examples of cyclic, non-cyclic  
& non-cyclic  $C_4F_8O$  isomers (refs at end).



This latest report (2020) now seems to be the only one easily accessible

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



Environment  
Report  
2021-2022



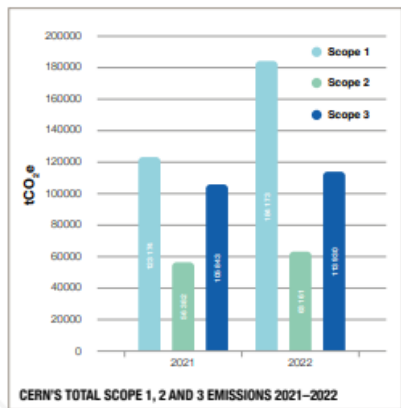
GROUP	GASES	ICO <sub>y</sub> 2021	ICO <sub>y</sub> 2022
Perfluorocarbons (PFCs)	CF <sub>4</sub> , C <sub>2</sub> F <sub>6</sub> , C <sub>3</sub> F <sub>8</sub> , C <sub>4</sub> F <sub>10</sub> , C <sub>6</sub> F <sub>14</sub>	55 921	68 989
Hydrochlorofluorocarbons (HCFCs)	HFC-23 (CHF <sub>3</sub> ) HFC-32 (CHF <sub>2</sub> ) HFC-134a (C <sub>2</sub> H <sub>2</sub> F <sub>4</sub> ) HFC-404a HFC-407c HFC-410a HFC-507	38 557	66 211
Other F-gases	SF <sub>6</sub> , NF <sub>3</sub>	18 838	18 355
Hydrofluorolefins (HFO)/HFCs	R-449 R1234ze NOVEC 649		
	CO <sub>2</sub>	13 771	10 419
<b>Total Scope 1</b>		<b>123 174</b>	<b>184 173</b>

R449: (CFH blend) GWP=1397  
R1234 (HFO): GWP = 7  
NOVEC 649 (C<sub>6</sub>F<sub>12</sub>O): GWP=0

# EMISSIONS

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

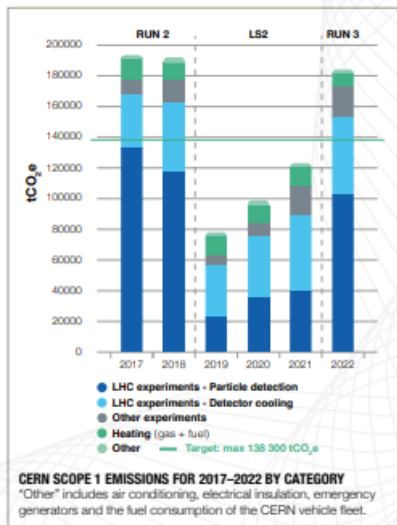
CERN reports on all emissions over which it has operational control. CERN's greenhouse gas emissions are estimated in accordance with the internationally recognised methodology of the Greenhouse Gas Protocol, which categorises such emissions into three "scopes". Scope 1 refers to the direct emissions resulting from an organisation's facilities and vehicles, while scope 2 refers to indirect emissions related to the generation of electricity, steam, heating or cooling purchased for an organisation's own use. Scope 3 refers to all other indirect emissions occurring upstream and downstream of an organisation's activities, such as business travel, personnel commutes, catering and procurement.



## DIRECT EMISSIONS – SCOPE 1

CERN's direct greenhouse gas emissions (scope 1) arise from the Laboratory's industrial infrastructure and on-site activities. Approximately 90% of CERN's scope 1 emissions come from its experiments. These use a wide range of gas mixtures for particle detection and detector cooling, including fluorinated gases (F-gases) which have a high global warming potential (GWP) and therefore account for about 78% of the Organization's direct emissions. The large experiments represent the main focus of CERN's efforts to mitigate its greenhouse gas emissions. The main gases used are HFCs, PFCs and SF<sub>6</sub> for particle detection, PFCs and HFCs for detector cooling and HFOs/HFCs for standard air conditioning systems. SF<sub>6</sub> is also used for electrical insulation in power supply systems.

With the gradual restart of the accelerator complex in 2021 ready for the launch of Run 3 of the LHC in mid-2022, the total amount of scope 1 greenhouse gas emissions was higher than in the period 2019–2020, when the accelerators were not running, namely 123 174 and 184 173 tonnes of CO<sub>2</sub> equivalent (tCO<sub>2</sub>e) in 2021 and 2022 respectively. CERN continuously improves its management, traceability and monitoring of F-gases, notably thanks to the awareness raised among stakeholders by the Working Group on F-Gases, which completed its work in 2021. In the reporting period, the large experiments have improved their approach and to minimise emissions, as reported below. Test facilities and other, smaller experiments have also improved their ability to trace emissions and are therefore now also included in the calculations for 2021 and 2022 to provide a complete view of scope 1 emissions.



## A STRATEGY TO REDUCE SCOPE 1 EMISSIONS

As for all other objectives that were set in the first environment report and whose original target date was 2024, the target has shifted concomitantly with the shift in the accelerator schedule. CERN's objective is therefore to reduce its scope 1 emissions by 28% by the end of Run 3 (baseline: 2018).

The current strategy to optimise the use of gases in the experiments rests on the following pillars: gas recirculation, gas recovery and the search for more environmentally friendly alternatives to the gases currently used. During Run 2 of the Large Hadron Collider (LHC), CERN tested a prototype plant for the recuperation of HFC-134a gas using a real detector. The results show a recovery efficiency of close to 80%. An updated prototype has been finalised and will be operational in the CMS experiment by March 2023.

A new CF<sub>4</sub> recovery plant was designed, built and successfully implemented for the RICH2 detector in the LHCb experiment.

Intense R&D activity is under way to identify possible alternatives to the greenhouse gases currently used in particle detection. New gases with a lower GWP, as well as the partial replacement of HFC-134a with CO<sub>2</sub>, are currently being tested for the future.

The main contributors to CERN's F-gas emissions are small leaks in the detectors caused by their light construction, which is dictated by the need to ensure that they fit inside the compact spaces that house them. As leaks occur regularly, systematic leak-repair campaigns are organised to ensure that they are contained and minimised. The leak-repair campaign launched by the ATLAS and CMS experiments during the second long shutdown (LS2) progressed well in the reporting period. It will continue in a later shutdown, when access will be possible again. Both experiments continued to invest in R&D to reduce detector leaks and prepare for a transition from PFCs to CO<sub>2</sub> cooling.

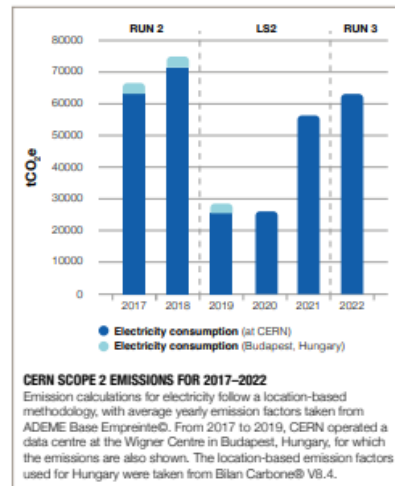
GROUP	GASES	100 <sub>e</sub> 2021	100 <sub>e</sub> 2022
Perfluorocarbons (PFCs)	CF <sub>4</sub> , C <sub>2</sub> F <sub>6</sub> , C <sub>3</sub> F <sub>8</sub> , C <sub>2</sub> F <sub>4</sub> , C <sub>2</sub> F <sub>2</sub>	55 921	68 989
Hydrochlorofluorocarbons (HFCs)	HFC-23 (CHF <sub>3</sub> ), HFC-32 (CH <sub>2</sub> F <sub>2</sub> ), HFC-134a (C <sub>2</sub> H <sub>2</sub> F <sub>4</sub> ), HFC-404a, HFC-407c, HFC-410a, HFC-507	36 557	86 211
Other F-gases	SF <sub>6</sub> , NF <sub>3</sub>	16 838	18 355
Hydrofluorolefins (HFO)/HFCs	R-449, R1234ze, NOVEC 649	86	199
	CO <sub>2</sub>	13 771	10 419
<b>Total Scope 1</b>		<b>123 174</b>	<b>184 173</b>

## BREAKDOWN OF SCOPE 1 EMISSIONS BY GAS TYPE 2021-2022

The 100<sub>e</sub> values have been calculated based on the real consumption of the different gases, weighted by their GWP. The GWP is based on the IPCC Fourth Assessment Report, 2007 (AR4), which is also the reference used in EU Regulation 517/2014 on fluorinated greenhouse gases.

## INDIRECT EMISSIONS – SCOPE 2

The total amount of scope 2 greenhouse gas emissions due to CERN's electricity consumption was 56 382 and 63 161 tCO<sub>2</sub>e in 2021 and 2022 respectively. EDF, CERN's principal electricity supplier, generates low-carbon electricity, mainly of nuclear origin, which contributes to keeping energy-related emissions relatively low. In this report, CERN reviewed the CO<sub>2</sub> emission factors that it applies in order to ensure that the figures quoted remain as accurate as possible. For CERN's internal purposes, both the market-based and the location-based methodologies of the Greenhouse Gas (GHG) Protocol are followed. Market-based emission factors take into account the actual sources of purchased energy. The location-based methodology uses emission factors that provide an average of the emissions from all power sources within a specific geographic region over a given period of time. The results of the location-based methodology are provided in this report, with calculations based on average yearly emission factors taken from ADEME Base Empreinte®. All years in the period 2017-2022 have been recalculated, as shown in the graph.



**But no mention at all of the ATLAS ultrasonic fluorocarbon leak monitor system !**

DRD4 WG 2 meeting: radiator gases May 17 2024



CERN  
CH1211 Geneva 23  
Switzerland

EN Engineering Department

EDMS NO.	REV.	VALIDITY
1751219	1.0	Released

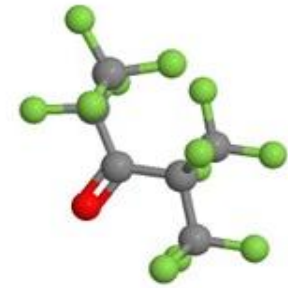
  

REFERENCE
2017-334

Date: 2017-12-22

Technical Note

NOVEC Fluids Qualification Report



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

# CERN has tested NOVEC 649

Equivalent radiation stability to  $C_6F_{14}$

used as liquid coolant in all LHC experiments;  
(Also non-flammable, non-toxic,  
dielectric, non- $O_3$  depleting);

( $C_6F_{12}O$ ) needs dessicants, but standard molecular sieves,  
activated-C OK: chosen SiPM coolant; LHCb Sci-Fi tracker



$C_6F_{14}$   
( $GWP_{20} = 5890$ )  
[16]

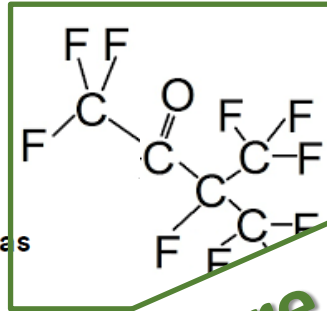
# Analogy: a Fluoroketone ( $C_nF_{2n}O$ ) replacement for a saturated fluorocarbon ( $C_nF_{(2n+2)}$ )

Thermophysical Properties of NOVEC 649 ( $C_6F_{12}O$ ) &  $C_6F_{14}$   
(at 25°C except where noted)

Fluid thermophysical property	NOVEC 649: $C_2F_5C(O)CF(CF_3)_2$ Perfluoro-2-methyl-3-pentanone ( $C_6F_{12}O$ )	$C_6F_{14}$ (Perfluorohexane, Saturated fluorocarbon)
Boiling Point (°C)	97	76
Critical Temp (°C)	169	178
Critical Pressure (MPa)	1.87	1.89
Specific heat ( $J \cdot kg^{-1} \cdot K^{-1}$ )	1103	1050
Density ( $kg \cdot m^{-3}$ )	1610	1680
Kinematic viscosity (cSt)	0.42	0.4
Latent Heat ( $J \cdot kg^{-1}$ )	88	88
Vapour Pressure @ 25 °C (kPa)	40.4	30.9
Vapour Pressure @ 100 °C (kPa)	441	350
Water solubility (ppm <sub>w</sub> )	21	10

No reason why the parameters between other SFCs and same order FK analogs shouldn't be *similarly similar...*

# Another exciting example: Novec 5110: $C_5F_{10}O$ MW = 266: GWP <1



Technical Data

3M™ Novec™ 5110 Insulating Gas

Typical Physical Properties

3M™ Novec™ 5110 Insulating Gas

### Introduction

3M™ Novec™ 5110 Insulating Gas is a sustainable alternative to sulfur hexafluoride (SF<sub>6</sub>) for electrical insulation and arc quenching applications. It offers excellent dielectric properties at high temperatures and significant reductions in environmental impact and has a wide safety margin for workers when used as a dielectric medium for medium voltage applications. Typical applications include gas-insulated switchgear, line bushings, and other high-voltage intended applications.

As shown in the following table, the environmental benefits of Novec 5110 are significant.

At a given pressure (in pure form) Novec 5110 provides a significant safety margin for intended applications.

Physical Properties of Novec 5110 Gas

Physical Properties of Novec 5110 Gas (continued)

Novec 5110 consists of CF<sub>3</sub>C(O)CF(CF<sub>3</sub>)<sub>2</sub> (CAS No. 756-12-7).

Mixing potential here with currently-available low GWP Fluoro-ketone (C<sub>n</sub>F<sub>2n</sub>O): Blend with N<sub>2</sub> to match C<sub>4</sub>F<sub>10</sub> and/or CF<sub>4</sub> - refractivity?

Property	3M™ Novec™ 5110 Insulating Gas	SF <sub>6</sub>
Boiling Point	-66°C	80.4°F
Freezing Point	-166°F	-166°F
Condensation Point	295°F	295°F
Gas Density at 1 bar	2.14 MPa	311 psia
Gas Density at 14.5 psia	10.7 kg/m <sup>3</sup> (at 1 bar)	0.67 lb/ft <sup>3</sup> (at 14.5 psia)
Dielectric Strength	93.8 kPa	13.6 psia
Breakdown Voltage (per disk electrodes)	18.4 at 1 bar over 2.5 mm gap	18.4 at 14.5 psia over 0.1 inch gap

Environmental Properties	3M™ Novec™ 5110 Insulating Gas	SF <sub>6</sub>
Atmospheric Lifetime (years)	0.04	3,200
Global Warming Potential (100-yr ITH, IPCC 2013 method)	<1	23,500
Ozone Depletion Potential (CFC-11 = 1)	0	0

As the Novec Insulating Gases are mixed with an inert gas (or gases) the reduction in GHG emissions is significant compared to installations using SF<sub>6</sub>.

Gas formulation	Novec 5110 Gas (5.0 mole %) in Air	100% SF <sub>6</sub>
Gas pressure (bar)	6.5	4
Gas density at 25°C (kg/m <sup>3</sup> )	10.7	23.6
Composite GWP of gas mixture	<1*	23,500
GWP reduction compared to SF <sub>6</sub>	99.99%	-
GHG emissions (MT CO <sub>2</sub> e/m <sup>3</sup> )	0.003**	554
GHG emissions reduction (i.e. CO <sub>2</sub> e reduction)	99.99%	-

\* GHG emission reduction takes into account the GWP and reduced density of the gas mixtures  
\*\* GWP<sub>Mixture</sub> = Σ(x<sub>i</sub> × GWP<sub>i</sub>)



**So why are spurred fluoro-  
ketones**

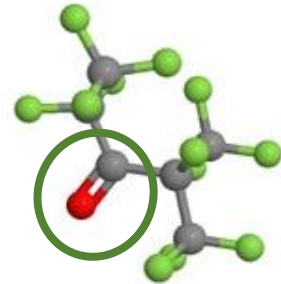
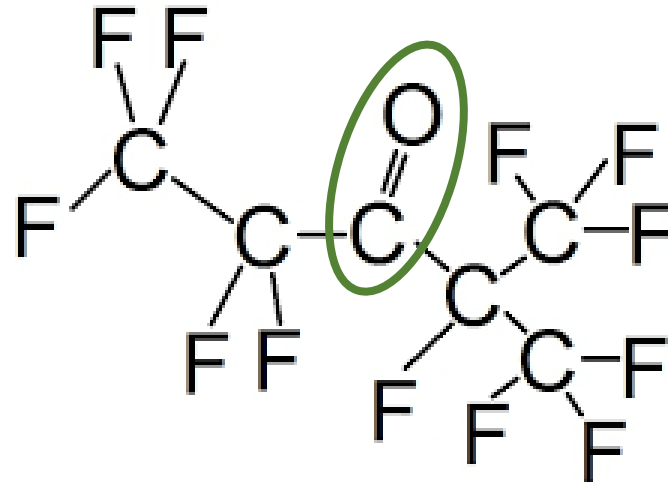


**potential substitutes for**

**saturated fluorocarbons?**



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



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

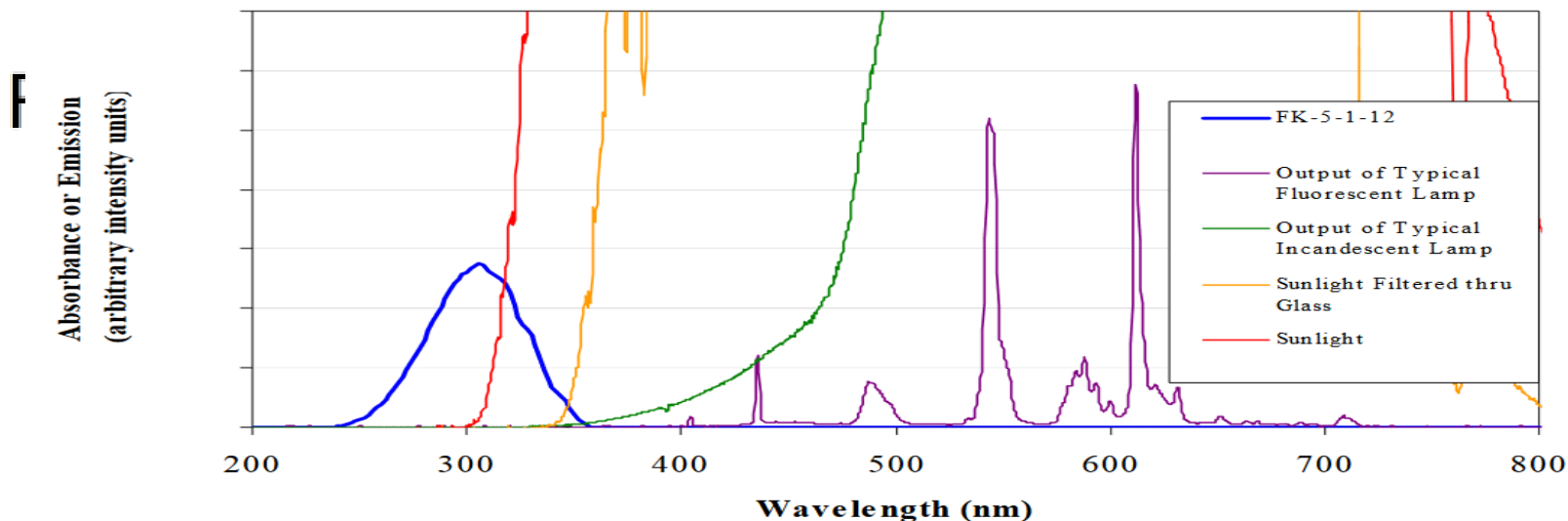
**A: Structure!:** a *double-bonded oxygen atom on a peripheral spur* of the molecule

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

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

[https://www.nist.gov/system/files/documents/el/fire\\_research/R0301570.pdf](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  $\lambda$  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>

**Positive and Negative  
experiences with  $C_4F_8O$  as a  
substitute for  $C_4F_{10}$   
Cherenkov radiator gas  
(BTeV and ALICE VHMPID)**



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**NUCLEAR  
INSTRUMENTS  
& METHODS  
IN PHYSICS  
RESEARCH**  
Section A

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## Beam test of a C<sub>4</sub>F<sub>8</sub>O-MAPMT RICH prototype

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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, C<sub>4</sub>F<sub>8</sub>O, 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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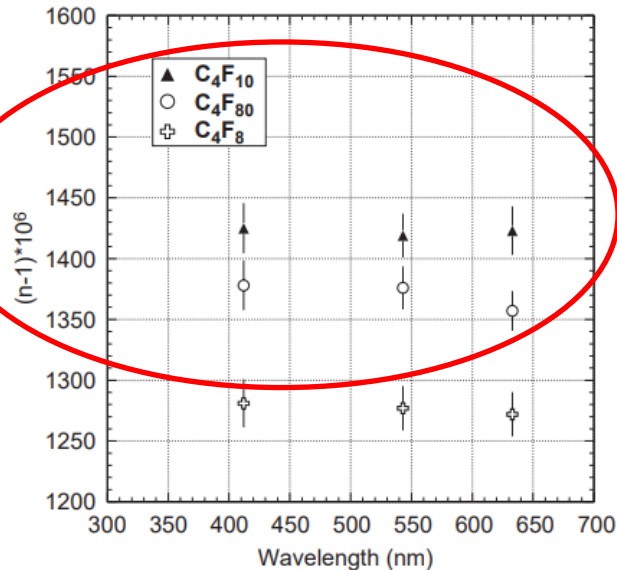
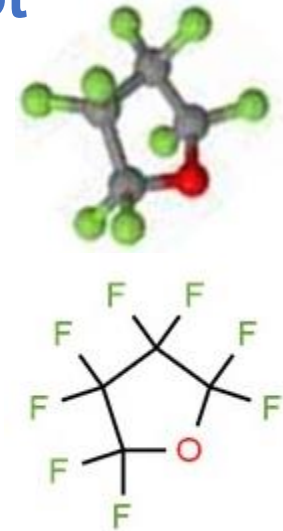


Fig. 5. Measurements of refraction indices of various gases as a function of laser light wavelength.

We then filled the gas tank with C<sub>4</sub>F<sub>8</sub>O. This is a replacement gas for C<sub>4</sub>F<sub>10</sub>, which was previously used in many RICH detectors. The industrial process at 3M yielding C<sub>4</sub>F<sub>10</sub> 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 C<sub>4</sub>F<sub>8</sub>O 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 distributor<sup>2</sup> the gas is 99.6% pure. The impurities consist mostly of the isomer of the main molecule (the latter has a cyclic structure: −CF<sub>2</sub>−CF<sub>2</sub>−O−CF<sub>2</sub>−CF<sub>2</sub>−) and other perfluorocarbons (freons). Non-perfluorocarbons are less than 0.05% of the volume. We measured the refraction index of C<sub>4</sub>F<sub>8</sub>O, C<sub>4</sub>F<sub>10</sub> and C<sub>4</sub>F<sub>8</sub> at 3 visible wavelengths using lasers and Michelson interferometry. The results are shown in Fig. 5. The refraction index of C<sub>4</sub>F<sub>8</sub>O is only slightly smaller than that of C<sub>4</sub>F<sub>10</sub>.

The test beam data with C<sub>4</sub>F<sub>8</sub>O 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 C<sub>4</sub>F<sub>8</sub>O gas was used as Cherenkov radiator for the first time and proved to be a suitable replacement for C<sub>4</sub>F<sub>10</sub>. 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. Menea, R. Mountain, H. Muramatsu, R. Nandakumar, L. Redjimi, K. Randrianarivony, S. Stone, R. Sia, J. Wang and H. Zhang.



# Shapes of $C_nF_{2n}O$ molecules and GWP: *Perfluortetrahydrofuran – The BTeV choice*

**Abstract.** The first atmospheric observations of octafluorooxolane (octafluorotetrahydrofuran,  $c\text{-}C_4F_8O$ ), a persistent greenhouse gas, are reported. In addition, a complementary laboratory study of its most likely atmospheric loss processes, its infrared absorption spectrum, and global warming potential (GWP) are reported. First atmospheric measurements of  $c\text{-}C_4F_8O$  are provided from the Cape Grim Air Archive ( $41^\circ$  S, Tasmania, Australia, 1978–present), supplemented by two firm air samples from Antarctica, in situ measurements of ambient air at Aspendale, Victoria ( $38^\circ$  S), and a few archived air samples from the Northern Hemisphere. The atmospheric abundance in the Southern Hemisphere has monotonically grown over the past decades and leveled at 74 ppq (parts per quadrillion, femtomole per mole in dry air) by 2015–2018. The growth rate of  $c\text{-}C_4F_8O$  has decreased from a maximum in 2004 of  $4.0$  to  $< 0.25$  ppq yr $^{-1}$  in 2017 and 2018. Using a 12-box atmospheric transport model, globally averaged yearly emissions and abundances of  $c\text{-}C_4F_8O$  are calculated for 1951–2018. Emissions, which we speculate to derive predominantly from usage of  $c\text{-}C_4F_8O$  as a solvent in the semiconductor industry, peaked at  $0.15$  ( $\pm 0.04$ ,  $2\sigma$ ) kt yr $^{-1}$  in 2004 and have since declined

to  $< 0.015$  kt yr $^{-1}$  in 2017 and 2018. Cumulative emissions over the full range of our record amount to 2.8 (2.4–3.3) kt, which correspond to 34 Mt of CO $_2$ -equivalent emissions. Infrared and ultraviolet absorption spectra for  $c\text{-}C_4F_8O$  as well as the reactive channel rate coefficient for the O( $^1D$ ) +  $c\text{-}C_4F_8O$  reaction were determined from laboratory studies. On the basis of these experiments, a radiative efficiency of  $0.430$  W m $^{-2}$  ppb $^{-1}$  (parts per billion, nanomol mol $^{-1}$ ) was determined, which is one of the largest found for synthetic greenhouse gases. The global annually averaged atmospheric lifetime, including mesospheric loss, is estimated to be  $> 3000$  years. GWPs of 8975, 12 000, and 16 000 are estimated for the 20-, 100-, and 500-year time horizons, respectively.

<https://repository.library.noaa.gov/044ed5ad-93ae-40e3-9420-d78a4729ff0f>

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# Shapes of $C_nF_{2n}O$ molecules and GWP:

## Octafluortetrahydrofuran – the probable ALICE VHMPID config

Nuclear Instruments and Methods in Physics Research A 732 (2013) 361–365



### R&D studies of a RICH detector using pressurized $C_4F_8O$ radiator gas and a CsI-based gaseous photon detector

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<sup>k</sup>Eotvos University, Budapest, Hungary

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#### ARTICLE INFO

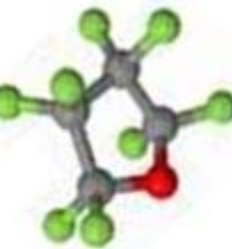
Available online 30 August 2013

Keywords:

RICH  
Cherenkov radiator  
Pressurized radiator gas  
Gaseous photodetector  
CsI photoconverter

#### ABSTRACT

We report on studies of layout and performance of a new Ring Imaging Cherenkov detector using for the first time pressurized  $C_4F_8O$  radiator gas and a photon detector consisting of a MWPC equipped with a CsI photocathode. In particular, we present here the results of beam tests of a MWPC having an adjustable anode-cathode gap, aiming at the optimization of single photoelectron detection and Cherenkov angle resolution. This system was proposed as a Very High Momentum Particle Identification (VHMPID) upgrade for the ALICE experiment at LHC to provide charged hadron track-by-track identification in the momentum range 5–25 GeV/c.



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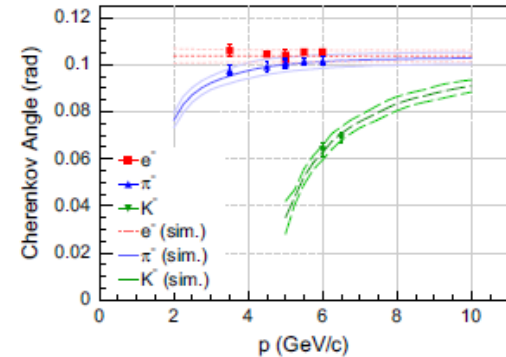


Fig. 11. Testbeam results for the Cherenkov angle as a function of the particle momentum, drawn together with simulated distributions for different particle species, for  $C_4F_8O$  radiator gas at 3.5 atm.

#### 5. Conclusions

An intense R&D campaign including beam tests has been carried out to study innovative solutions, adopted to meet the new requirements for PID in the 5–25 GeV/c momentum range and the need for a strongly reduced depth to allow the combined integration with a calorimeter in the same acceptance. The performance dependence on pad size and anode-cathode gap of the CsI-based MWPC photon detector has been studied and the new layout has to be confirmed by simulations. For the first time a RICH prototype using  $C_4F_8O$  radiator gas at 3.5 atm has been successfully tested, validating both the application of such a gas as Cherenkov radiator in the UV range and the design concepts for pressurization and heating.

$C_4F_8O$  acquired from Synquest (FL,USA) : reported by A. di Mauro:

DRD4 WG 2 meeting: radiator gases May 17 2024

The ideal new radiator fluids would be the non-cyclic  $C_nF_{2n}O$  molecules with the same carbon order as  $CF_4$ ,  $C_4F_{10}$  if these become available.

**We should NOT be considering flammable gases or high pressure (large PV stored energy) gas radiators for underground areas (this is an even bigger “fantasy”).**

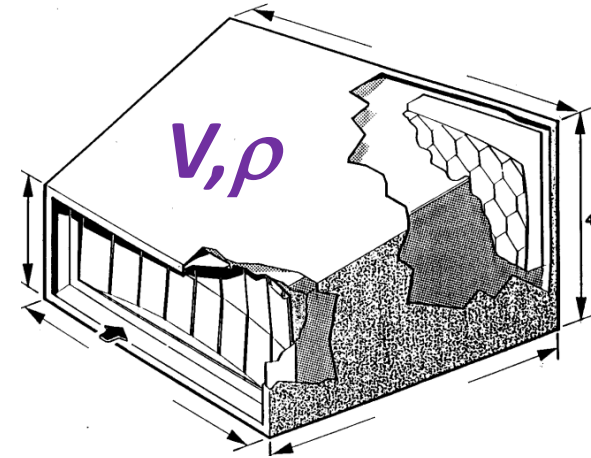
However in their absence we can blend NOVEC 5100 or even legacy high-order fluorocarbons at low conc. to reduce gas radiator GWP:

# Refractive index & GWP 'load' in a Cherenkov Gas Radiator

3 large RICH detectors currently in operation at CERN:  
using saturated fluorocarbon gas volumes ~ 50-100 m<sup>3</sup>:

C<sub>4</sub>F<sub>10</sub> (COMPASS, LHCb RICH 1):  $GWP_{20} = 4880$ ,

CF<sub>4</sub> (LHCb RICH 2):  $GWP_{20} = 6870$



A Cherenkov radiator vessel of volume  $V(m^3)$  filled with a blend of gases of densities  $\rho_i (kgm^{-3})$ , fractional concentrations  $w_i$  and individual  $GWP_i$  (tonnes CO<sub>2</sub> eq.) has a GWP environmental “load” (& release potential)  $L$  given by:

$$L = \frac{V}{1000} \sum_i (w_i \cdot \rho_i \cdot GWP_i) \quad (\text{tonnes CO}_2 \text{ eq.}) \quad [\text{Eq. (1)}]$$

The corresponding radiator gas mixture refractivity is given by :

$$(n-1)_{rad} = \sum_i (w_i \cdot (n-1)_i) \quad [\text{Eq. (2)}]$$

How to find the molar concentrations  $w_i$  of the constituents?

Use speed of sound measured in real-time  
 (traditionally also called “c” by acousticians to confuse things)  
 to get the molar concentrations of the gas components  $\omega_i$

$$c = \sqrt{\frac{\gamma RT}{M}} \quad \gamma_m = \frac{C_{pm}}{C_{vm}} = \frac{\sum_i \omega_i C_{p_i}}{\sum_i \omega_i C_{v_i}} \quad M = \sum_i \omega_i M_i \quad c = \sqrt{\frac{\sum_i \omega_i C_{p_i} RT}{\sum_i \omega_i C_{v_i} \sum_i \omega_i M_i}}$$

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

$$(n-1)_{rad} = \sum_i (\omega_i \cdot (n-1)_i)$$

to refractive index of the radiator gas in real-time along with  
 standard relativistic expressions to get from n to Cherenkov  $\gamma$   
 thresholds for different particle species and  $\beta = 1$  angle

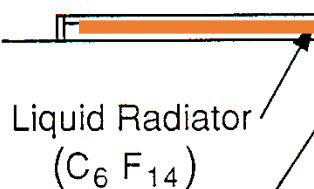
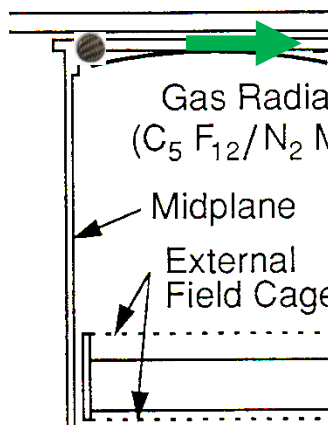
Real-time measurement of *speed of sound*  $c$  takes us via the relative  
 concentrations of the components to the *speed of light*  $\beta$  **and beyond!!**  
 in the radiator gas

Remembering the aim...(focus here on LHCb RICH2...)

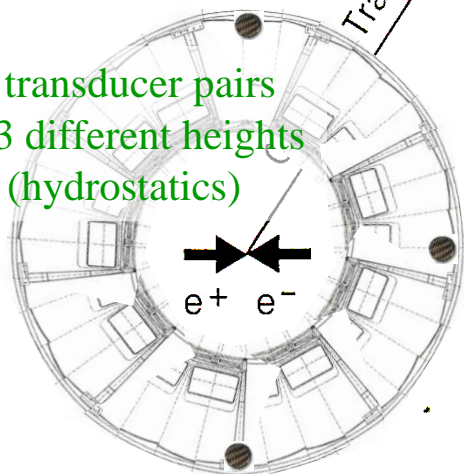
$$(488 \cdot 10^{-6})_{CF_4} = (\sim 1750 \cdot 10^{-6})_{C_5F_{100}} \cdot 0.12 + (300 \cdot 10^{-6})_{N_2} \cdot 0.88$$



# Historical: The SLD experience: barrel CRID gas radiators (1990s)



6 transducer pairs  
@ 3 different heights  
(hydrostatics)



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Research Section A: Accelerators, Spectrometers,  
Detectors and Associated Equipment

Volume 264, Issues 2–3, 15 February 1988, Pages 219–234



## A sonar-based technique for the ratiometric determination of binary gas mixtures ☆

G. Hallewell, G. Crawford \*\*, D. McShurley, G. Oxoby, R. Reif

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Received 25 March 1987, Revised 17 September 1987, Available online 28 October 2002.

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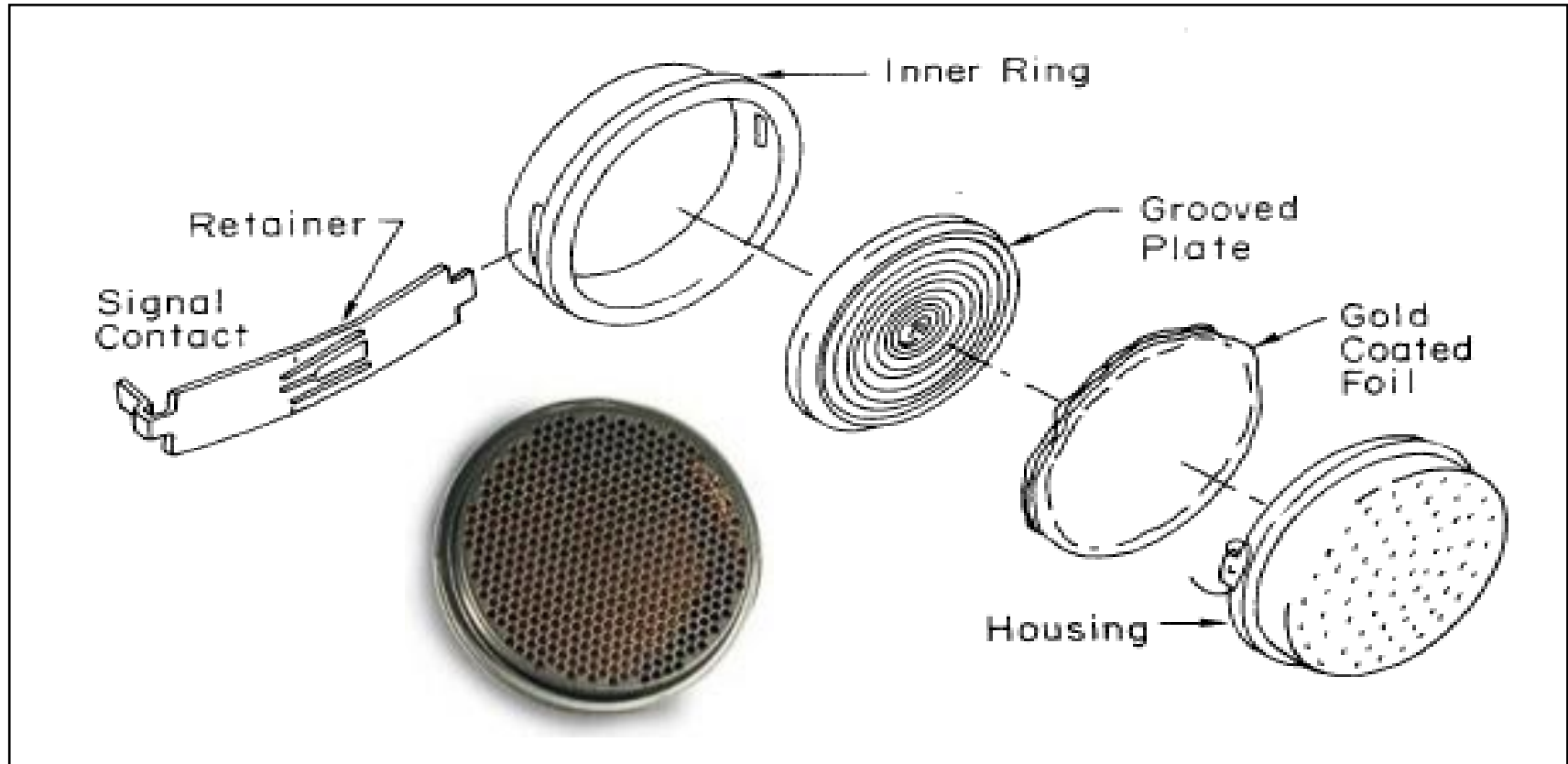
[https://doi.org/10.1016/0168-9002\(88\)90912-6](https://doi.org/10.1016/0168-9002(88)90912-6)

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### Abstract

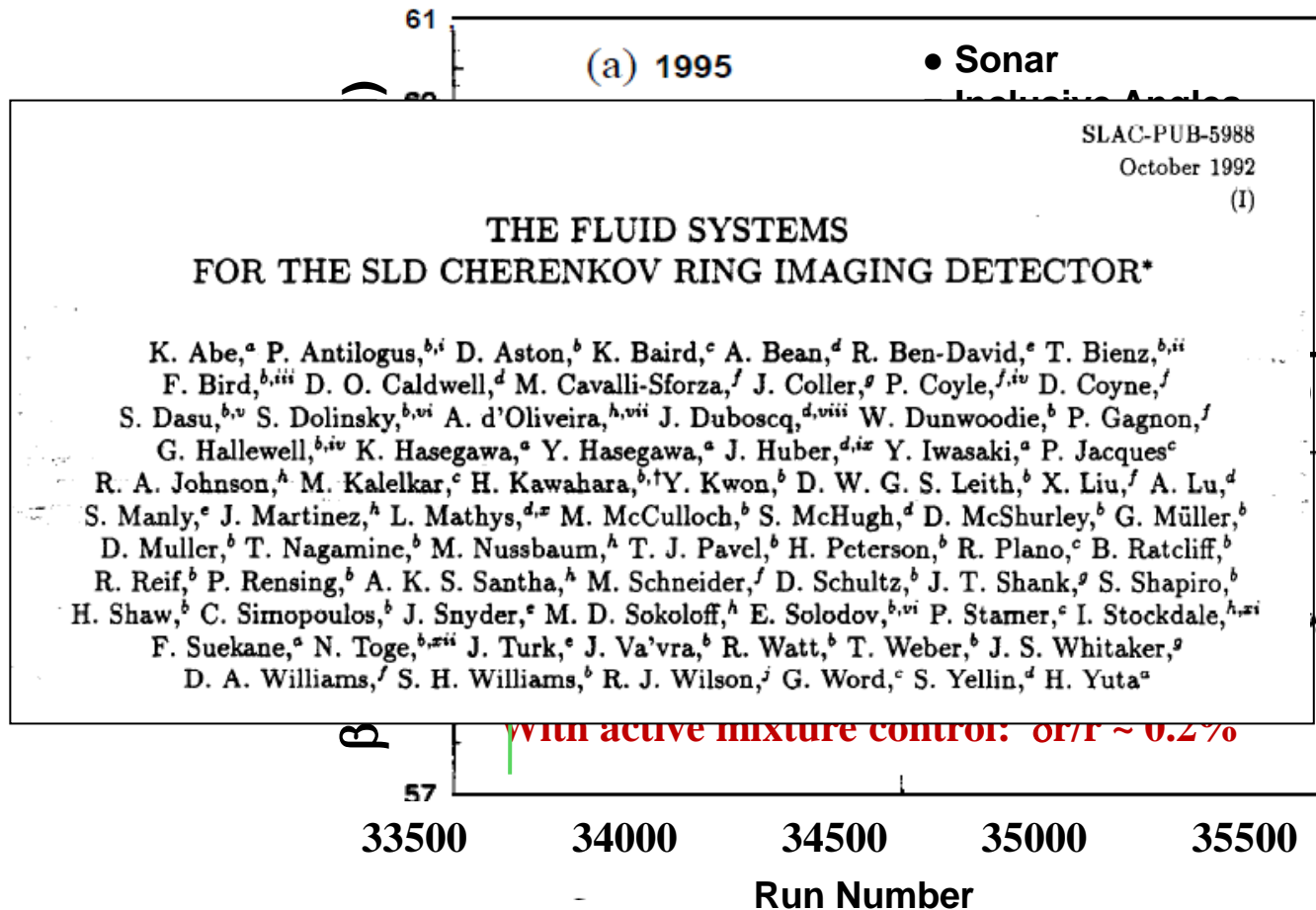
We have developed an inexpensive sonar-based instrument to provide a routine on-line monitor of the composition and stability of several gas mixtures having application in a Cherenkov Ring Imaging Detector. The instrument is capable of detecting small (<1%) fluctuations in the relative concentration of the constituent gases and, in contrast with some other gas analysis techniques, lends itself well to complete automation.

# Polaroid Capacitive transducer components



**Capacitive 350V activation/ bias → rapid response  
37mm diameter determines 50 kHz dominant frequency: can  
operate over wide pressure range (50mbar → >35 bar...)**

# Improvements in maintaining $C_5F_{12}/N_2$ refractive index through sonar-based active mixture control



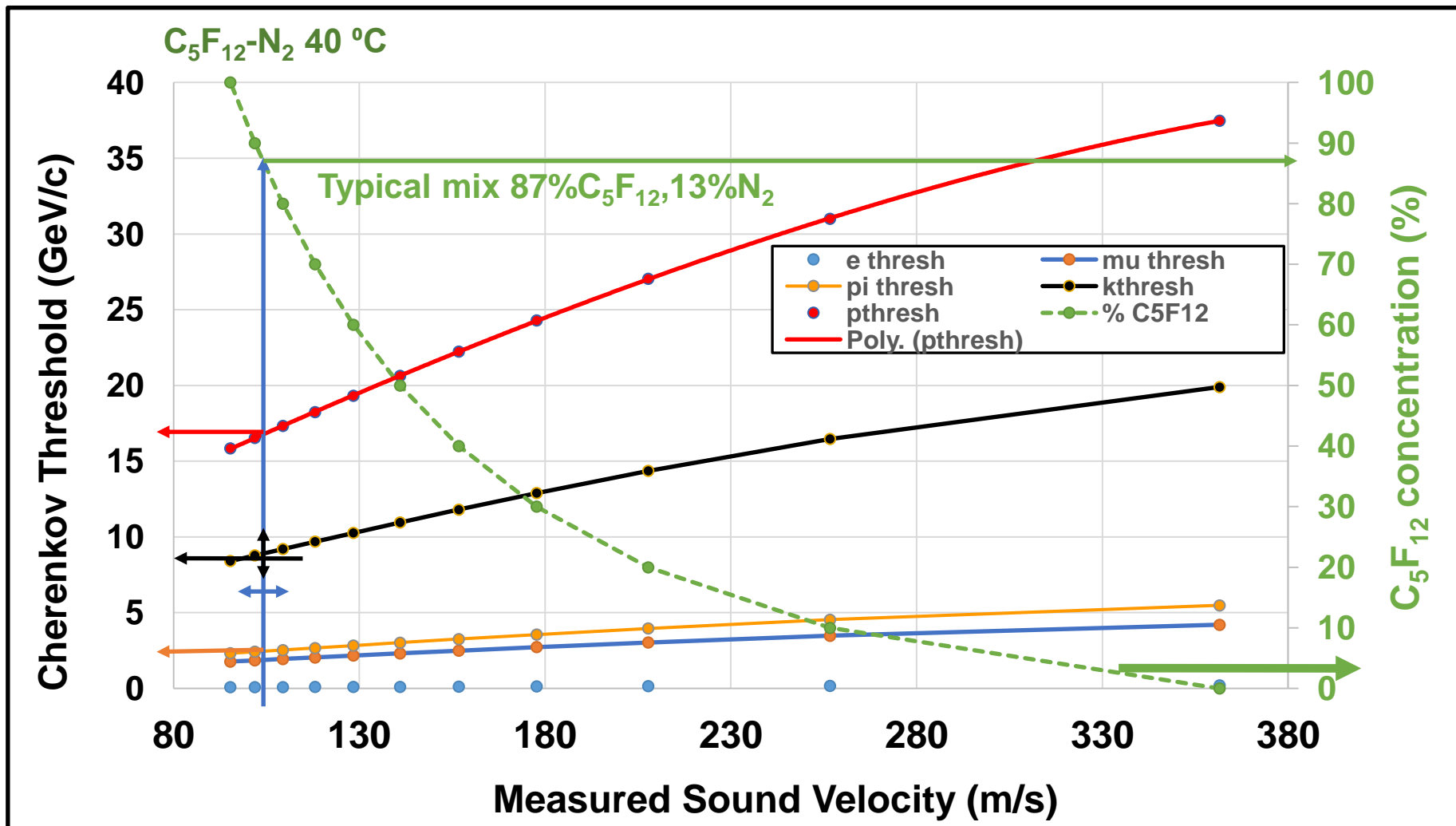
Before use of flowmeter analyzer in supply line

Using the flowmeter analyzer in supply line to modify the blend by hardwired 4-20mA link to mass flow controllers

Note: before and after blend stabilization sonar interpreted  $\beta=1$  radius agreed well with reconstructed radii!!

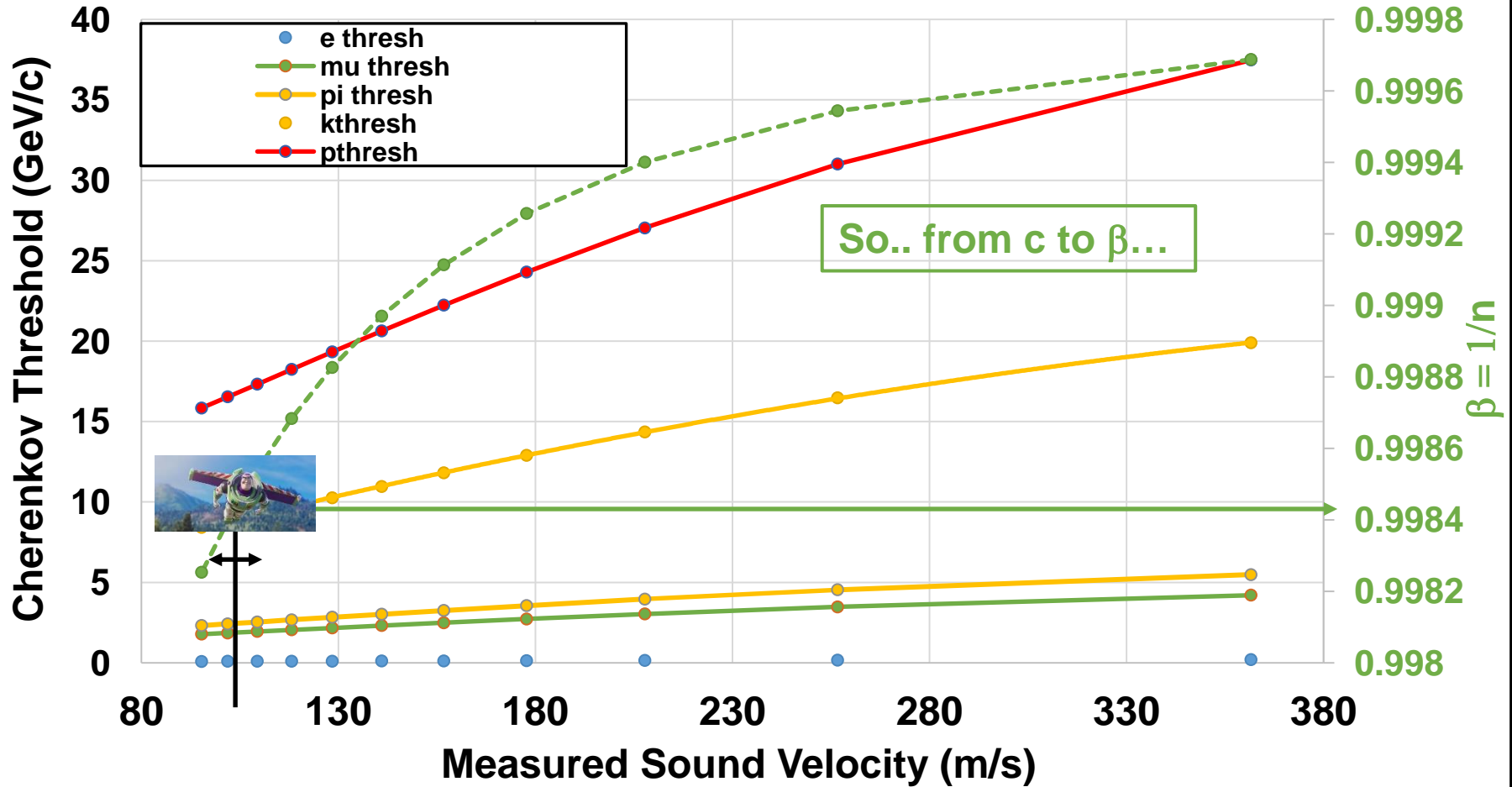
$\beta = 1$  Cherenkov angle comparison (1995-6 runs) between reconstructed ring data ( $\square$ ) in the SLD barrel CRID and angles from sonar-deduced refractive index corrected for atmospheric pressure ( $\bullet$ )

# SLD-CRID: Cherenkov threshold in $C_5F_{12}/N_2$ mixtures vs. measured speed of sound in radiator gas mixture (1)



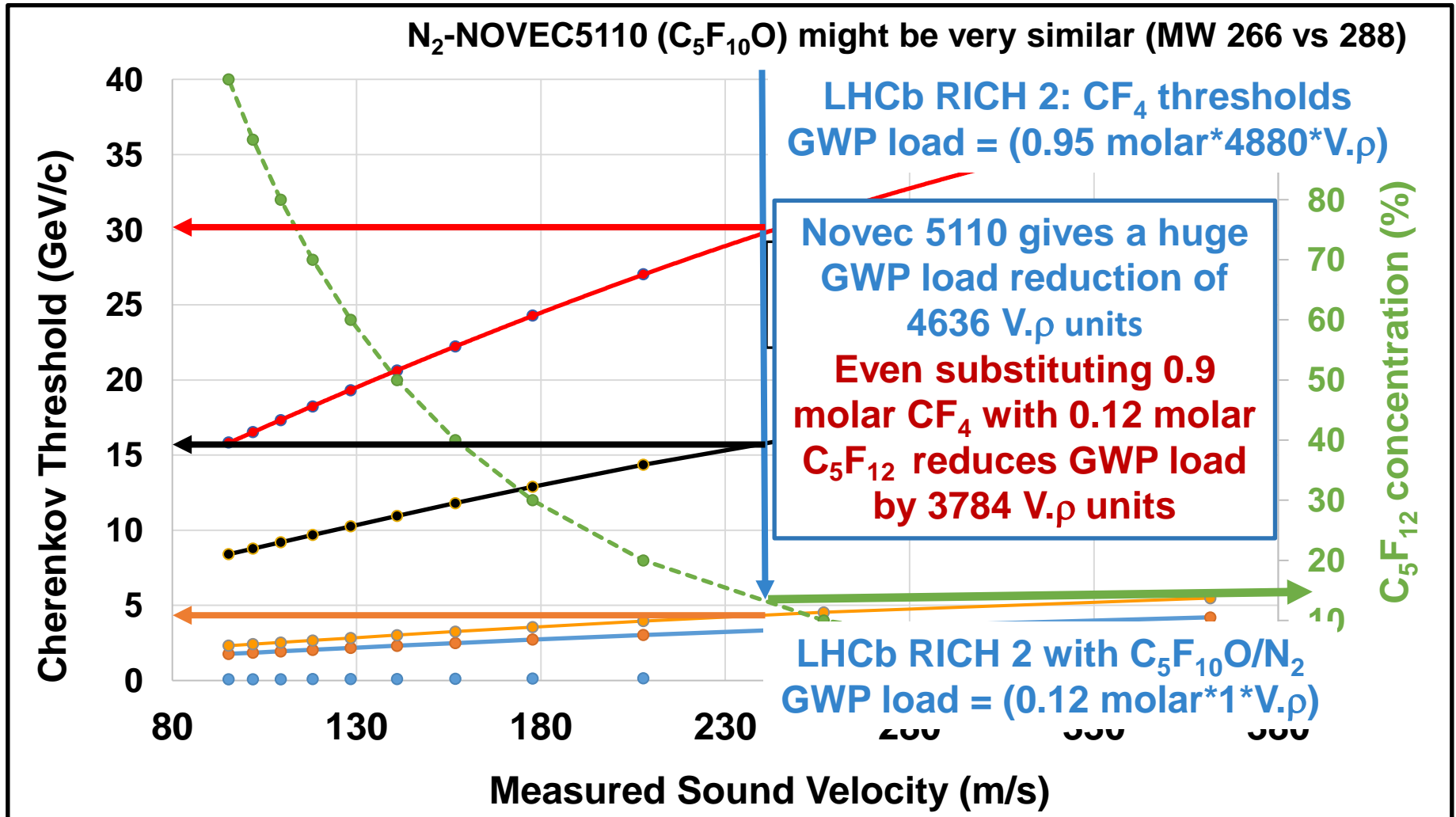
# SLD-CRID: Cherenkov threshold in $C_5F_{12}/N_2$ mixtures vs. measured speed of sound in radiator gas mixture (2)

$C_5F_{12}-N_2$  40 °C:  $N_2$ -NOVEC5110 ( $C_5F_{10}O$ ) might be very similar





# Cherenkov threshold in $C_5F_{12}/N_2$ mixtures and GWP load comparison with LHCb RICH2 (new vol.?)



**Table 1:** GWP loads of various SFCs and NOVEC 5110 blended with N<sub>2</sub> ((n-1) = 310.10<sup>-6</sup>) to match refractivity of CF<sub>4</sub> and C<sub>4</sub>F<sub>10</sub> assumed radiator volume: 100 m<sup>3</sup>

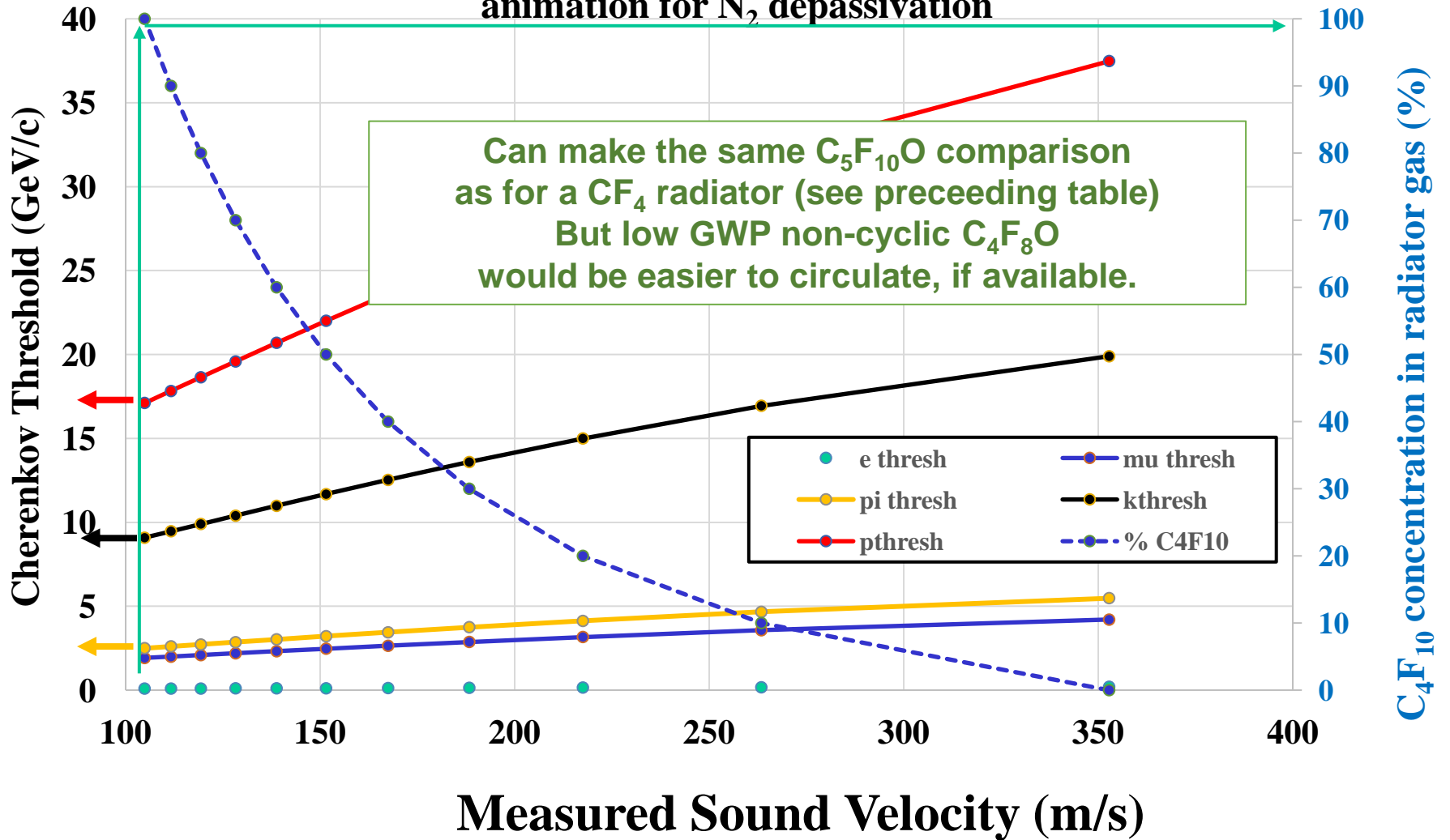
Base fluid	Base fluid density (1bar,25°C) kgm <sup>-3</sup>	Base fluid GWP (20-yr)	Component (n-1) (*10 <sup>6</sup> ) (@ nm)	% Blend with N <sub>2</sub> to match (n-1) CF <sub>4</sub>	GWP load (t.CO <sub>2</sub> )	% Blend with N <sub>2</sub> to match (n-1) C <sub>4</sub> F <sub>10</sub>	GWP load (t.CO <sub>2</sub> )
CF <sub>4</sub> LHCb RICH2	<b>3.56 [18]</b>	<b>4880 [16]</b>	<b>488 (180-310 nm) [19]</b>	<b>100</b>	<b>1737</b>	<b>not applicable</b>	<b>n/a</b>
CF <sub>2</sub> O	-			-		n/a	n/a
C <sub>2</sub> F <sub>6</sub>	5.63 [18]	8210 [16]	793 (180-310 nm) [19]	38.1	1762	not applicable	n/a
<i>Lin-C<sub>2</sub>F<sub>4</sub>O</i>	-			-		n/a	n/a
C <sub>3</sub> F <sub>8</sub>	7.75 [18]	6640 [16]	1180 (250 nm) [16]	21.4	1099	not applicable	n/a
<i>Lin-C<sub>3</sub>F<sub>6</sub>O</i>	-			-		n/a	n/a
C <sub>4</sub> F <sub>10</sub> LHCb RICH1	<b>9.97 [18]</b>	<b>6870 [16]</b>	<b>1450 (250 nm) [16]</b>	<b>16.3</b>	<b>1119</b>	<b>100</b>	<b>6849</b>
<i>Lin-C<sub>4</sub>F<sub>8</sub>O (Non-cyclic C<sub>4</sub>F<sub>8</sub>O)*</i>	9.5 (est.)	<i>Probably &lt; 1 (NOVEC 5110 Analogy)</i>	<i>1380 @ 400nm (based on 3M PFG-3480 c-C<sub>4</sub>F<sub>8</sub>O [7]: linear C<sub>4</sub>F<sub>8</sub>O not yet measured but assumed similar)</i>	18.4	0.18	112.7* (>100% would imply necessity of operating C <sub>4</sub> F <sub>8</sub> O at slight overpressure)	1.07
C <sub>5</sub> F <sub>12</sub>	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 <sub>5</sub> F <sub>10</sub> O	10.7 [13] (BP 27 °C at 1 bar)	<1 [13]	Not yet measured: probably around 1650 by analogy with C <sub>4</sub> F <sub>10</sub> and C <sub>4</sub> F <sub>8</sub> O ratio	<b>13.9</b>	<b>0.149</b>	85.2	0.91

Positions of presently *unavailable-in-bulk* C<sub>n</sub>F<sub>2n</sub>O fluids are shown in *italics*. Refractivities to match (CF<sub>4</sub> and C<sub>4</sub>F<sub>10</sub>) shown in **bold**. GWP loads and refractivities calculated using eqs. (1)-(3): assumed radiator volume: 100 m<sup>3</sup>

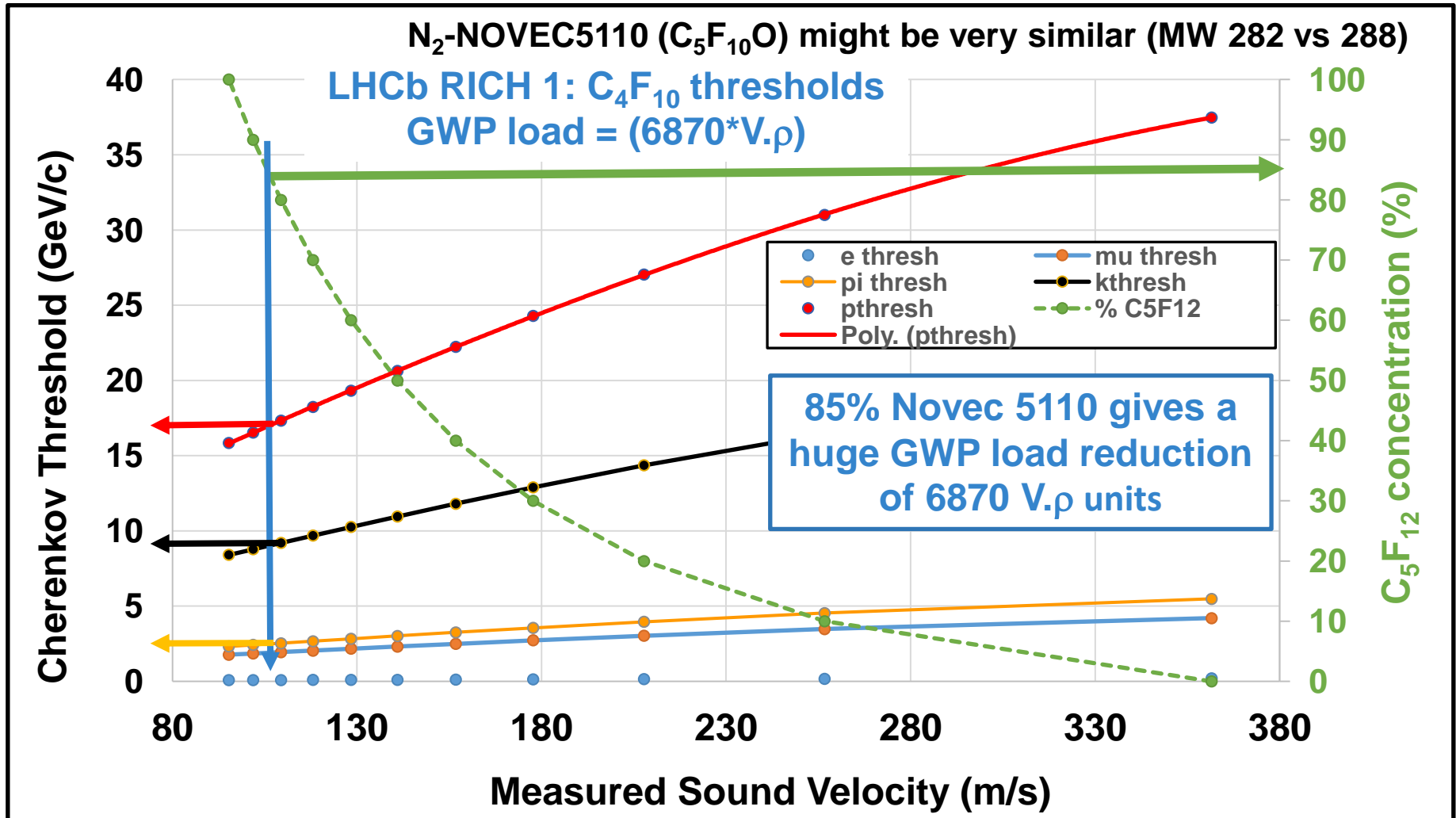
\*Made in research quantities by Synquest Inc. as isomers Heptafluorobutyryl fluoride **PN:** 2116-2-07 **CAS:** 335-42-2 Octafluoro-2-butanone **PN:** 2117-2-10 **CAS:** 337-20-2 & Heptafluoroisobutyryl fluoride **PN:** 2116-2-0A **CAS:** 677-84-9

# Situation for RICH radiators using $C_4F_{10}$ with $N_2$ passivant

e.g.: COMPASS, LHCb RICH 1:  $C_4F_{10}$ - $N_2$  @ 25 °C:  
animation for  $N_2$  depassivation



# Cherenkov threshold in $C_5F_{12}/N_2$ mixtures and GWP load comparison with LHCb RICH1 (new vol.?)



**Table 1:** GWP loads of various SFCs and NOVEC 5110 blended with N<sub>2</sub> ((n-1) = 310.10<sup>-6</sup>) to match refractivity of CF<sub>4</sub> and C<sub>4</sub>F<sub>10</sub> assumed radiator volume: 100 m<sup>3</sup>

Base fluid	Base fluid density (1bar,25°C) kgm <sup>-3</sup>	Base fluid GWP (20-yr)	Component (n-1) (*10 <sup>6</sup> ) (@ nm)	% Blend with N <sub>2</sub> to match (n-1) CF <sub>4</sub>	GWP load (t.CO <sub>2</sub> )	% Blend with N <sub>2</sub> to match (n-1) C <sub>4</sub> F <sub>10</sub>	GWP load (t.CO <sub>2</sub> )
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C <sub>3</sub> F <sub>8</sub>	7.75 [18]	6640 [16]	1180 (250 nm) [16]	21.4	1099	not applicable	n/a
Lin-C <sub>3</sub> F <sub>6</sub> O	-			-		n/a	n/a
C <sub>4</sub> F <sub>10</sub> LHCb RICH1	<b>9.97 [18]</b>	<b>6870 [16]</b>	<b>1450 (250 nm) [16]</b>	<b>16.3</b>	<b>1119</b>	<b>100</b>	<b>6849</b>
Lin-C <sub>4</sub> F <sub>8</sub> O (Non-cyclic C <sub>4</sub> F <sub>8</sub> O)*	9.5 (est.)	Probably < 1 (NOVEC 5110 Analogy)	1380 @ 400nm (based on 3M PFG-3480 c-C <sub>4</sub> F <sub>8</sub> O [7]: linear C <sub>4</sub> F <sub>8</sub> O not yet measured but assumed similar)	18.4	0.18	112.7* (>100% would imply necessity of operating C <sub>4</sub> F <sub>8</sub> O at slight overpressure)	1.07
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Positions of presently *unavailable-in-bulk* C<sub>n</sub>F<sub>2n</sub>O fluids are shown in *italics*. Refractivities to match (CF<sub>4</sub> and C<sub>4</sub>F<sub>10</sub>) shown in **bold**. GWP loads and refractivities calculated using eqs. (1)-(3): assumed radiator volume: 100 m<sup>3</sup>

\*Made in research quantities by Synquest Inc. as isomers Heptafluorobutryl fluoride **PN:** 2116-2-07 **CAS:** 335-42-2 Octafluoro-2-butanone **PN:** 2117-2-10 **CAS:** 337-20-2 & Heptafluoroisobutryl fluoride **PN:** 2116-2-0A **CAS:** 677-84-9

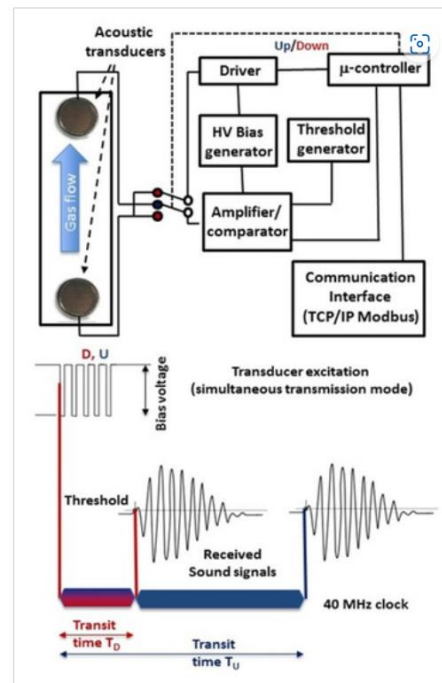
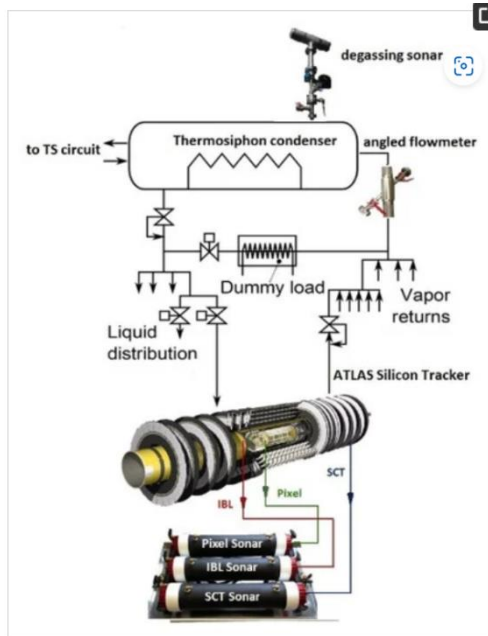
**Ultrasonic gas analysis in ATLAS:  
*the only fluorocarbon leak  
detection of its type at CERN***

*(a non-Cherenkov,  
environmental monitor,  
with extended analysis  
algorithm)...*



# Ultrasonic gas analysis in a process environment with multiple background gases

<https://www.mdpi.com/2410-390X/5/1/6>



Article

## Applications and Perspectives of Ultrasonic Multi-Gas Analysis with Simultaneous Flowmetry

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**Abstract:** We have developed ultrasonic instrumentation for simultaneous flow and composition measurement in a variety of gas mixtures. Flow and composition are respectively derived from measurements of the difference and average of sound transit times in opposite directions in a flowing process gas. We have developed a sound velocity-based algorithm to compensate for the effects of additional gases, allowing the concentrations of a pair of gases of primary interest to be acoustically measured on top of a varying baseline from 'third party' gases whose concentrations in the multi-gas mixture are measured by other means. Several instruments are used in the CERN ATLAS experiment. Three monitor  $C_3F_8$  (R218), and  $CO_2$  coolant leaks into  $N_2$ -purged environmental envelopes. Precision in molar concentration of better than  $2 \times 10^{-5}$  is routinely seen in mixtures of  $C_3F_8$  in  $N_2$  in the presence of varying known concentrations of  $CO_2$ . Further instruments monitor air ingress and  $C_3F_8$  vapor flow (at high mass flows around  $1.1 \text{ kg s}^{-1}$ ) in the 60 kW thermosiphon  $C_3F_8$  evaporative cooling recirculator. This instrumentation and analysis technique, targeting binary pairs of gases of interest in multi-gas mixtures, is promising for mixtures of anesthetic gases, particularly in the developing area of xenon anaesthesia.

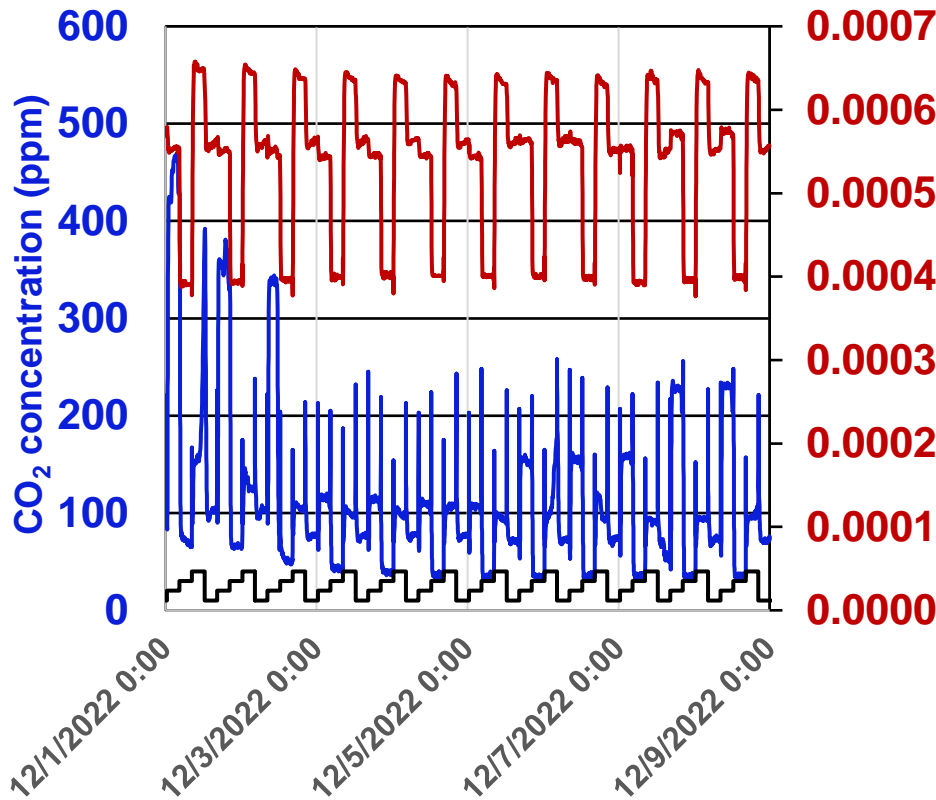
**Keywords:** ultrasonic gas analysis; ultrasonic flowmetry; leak detection; xenon anaesthesia

### 1. Introduction

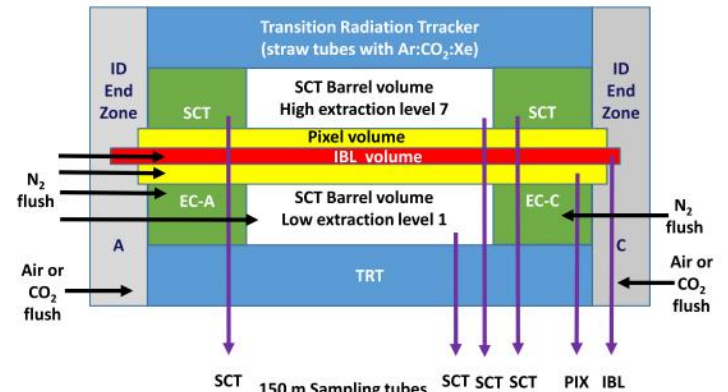
Continuous, real-time precision measurements of relative concentration of binary pairs of gases are required in many applications. The presence of other gases can however cause ambiguities in the measurement: a particular measured sound velocity can be the result of varying combinatorial concentrations of additional gases. Custom ultrasonic ("sonar") instruments have been developed [1] for real-time monitoring and measurement of binary gas mixtures in the ATLAS experiment at the CERN Large Hadron Collider (LHC). The ATLAS particle physics detector consists of a series of concentric sub-detectors, including a silicon charged particle tracking detector located near the LHC proton beam collision point. The silicon tracker is evaporatively cooled using octafluoropropane (R218:  $C_3F_8$ ) and  $CO_2$ , operating below  $-10^\circ\text{C}$  to reduce the effects of radiation damage. Three ultrasonic instruments monitor coolant leaks into the nitrogen-purged envelopes surrounding the

**Precision:  $10^{-5} C_3F_8$  into  $N_2$  at 1 bar**

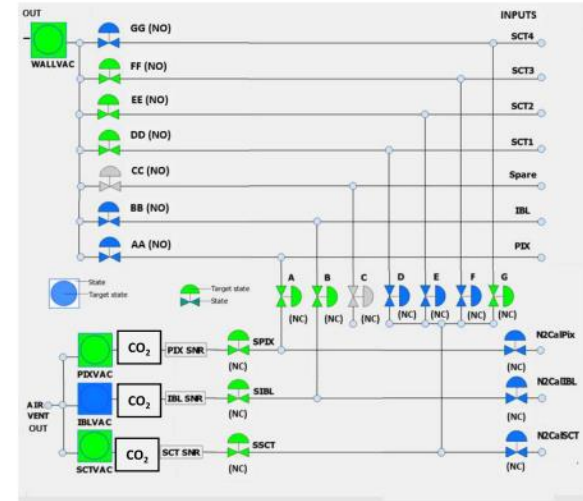
**Fig. 16** The coolant leak monitoring system of the ATLAS silicon tracker. Upper: gas sampling points in the nitrogen-purged environment volumes of the IBL, pixel and SCT sub-detectors. Lower: view of the arrangement of aspiration pumps, remote control selection valves and sonar tubes (Siemens synatic graphical user interface). SCT1-4 are sequentially sampled by SCTSNR in four-hour periods via remote control NC valves D-G



- CO2 concentration (ppm)
- Zone
- C3F8 concentration



C<sub>3</sub>F<sub>8</sub> concentration (%)



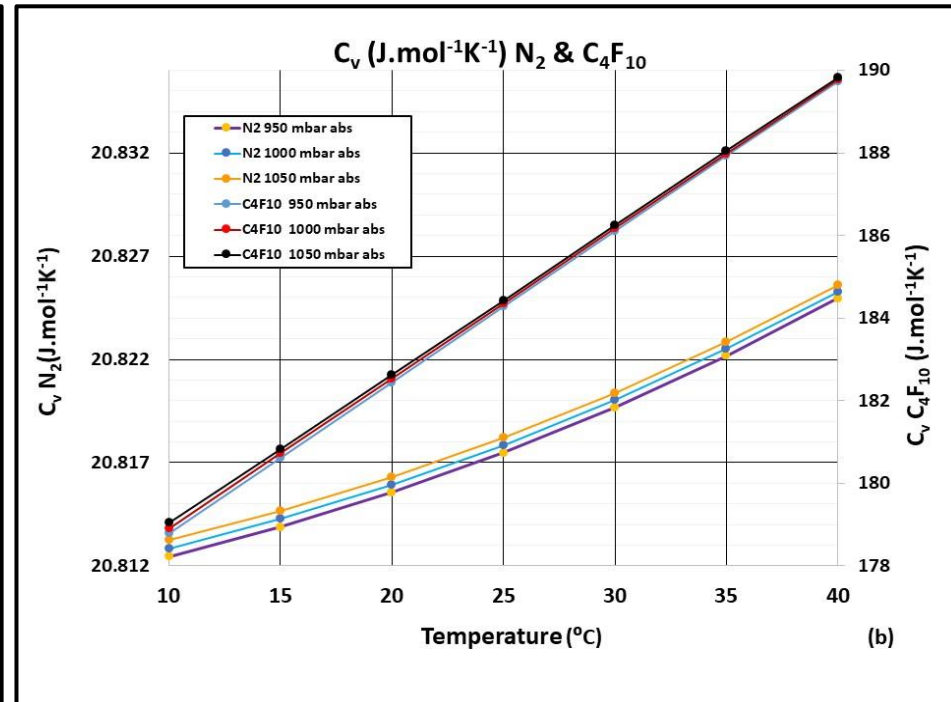
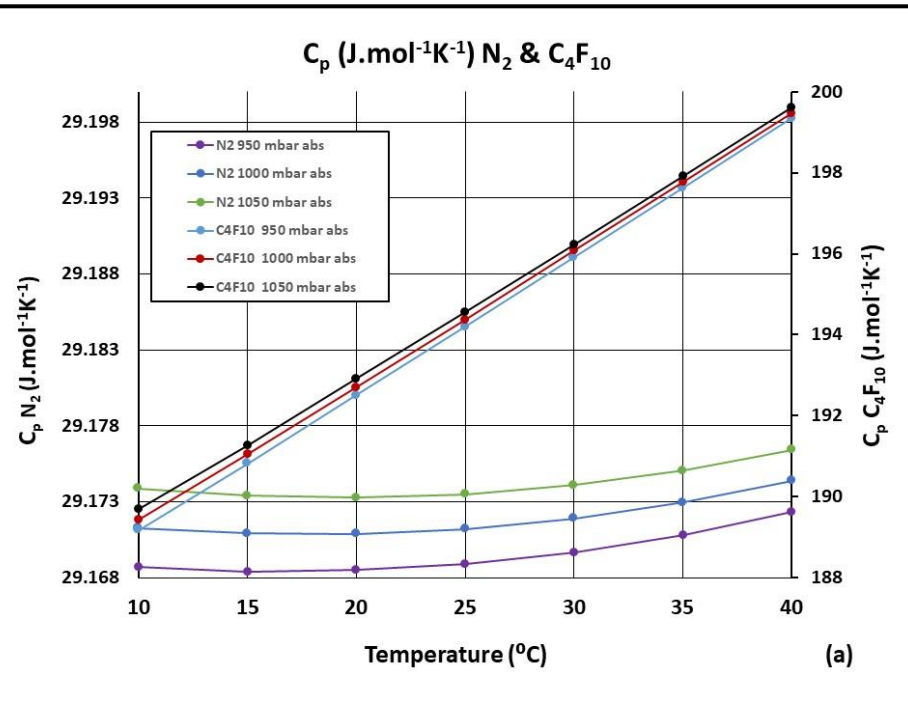
# Ultrasonic algorithm to find component molar concentrations

$$\omega_{i=1,2,\dots}$$

in gas blends

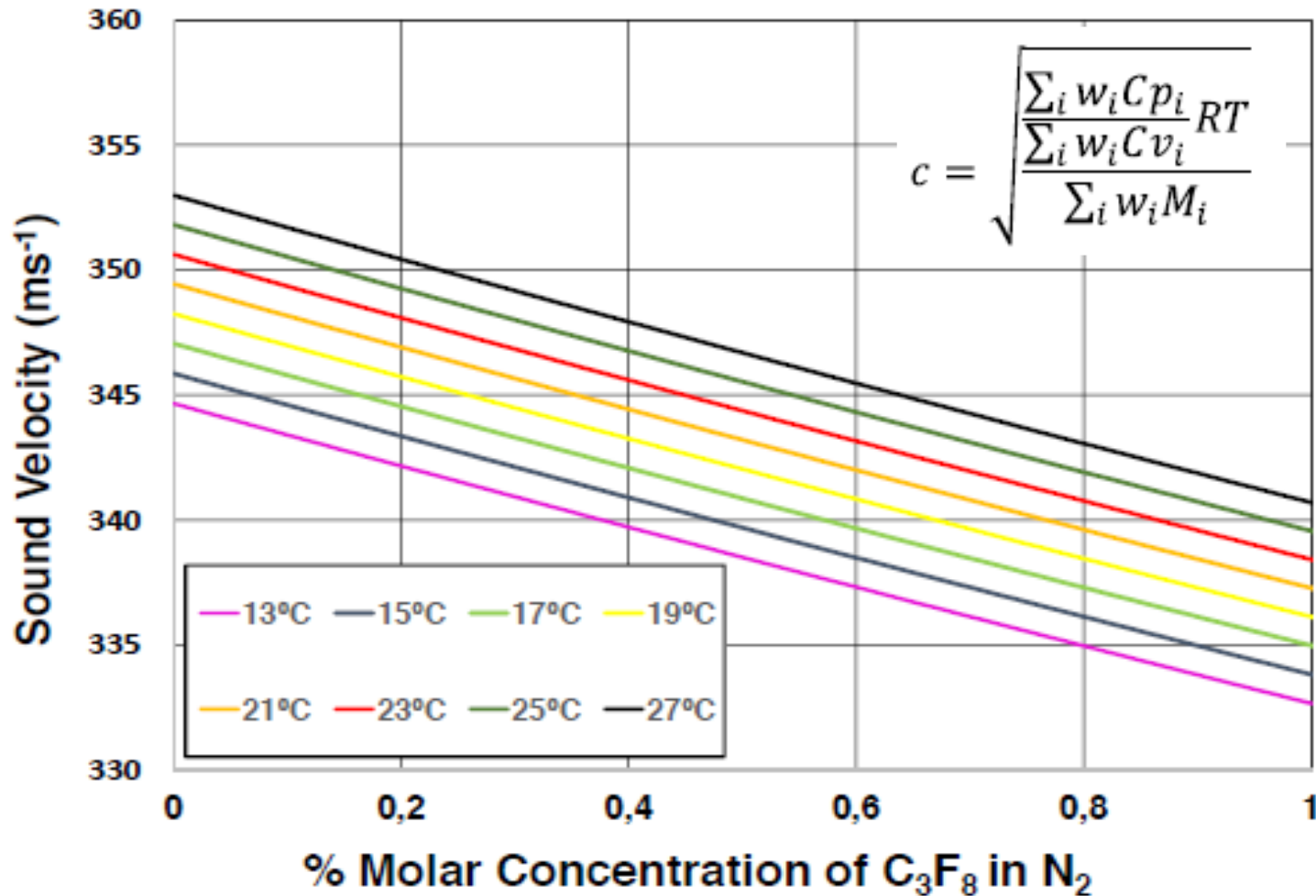
$$c = \sqrt{\frac{\gamma RT}{M}} \quad \gamma_m = \frac{C_{pm}}{C_{vm}} = \frac{\sum_i \omega_i C_{pi}}{\sum_i \omega_i C_{vi}} \quad M = \sum_i \omega_i M_i \quad c = \sqrt{\frac{\sum_i \omega_i C_{pi} RT}{\sum_i \omega_i M_i}}$$

**(1) Calculate data base of individual  $C_{Vi..n}$   $C_{Pi..n}$   
over expected T, P. range:  
Example here:  $C_3F_8$ : (mol. wt.) = 188 in  $N_2$  (mol. wt. = 28)**



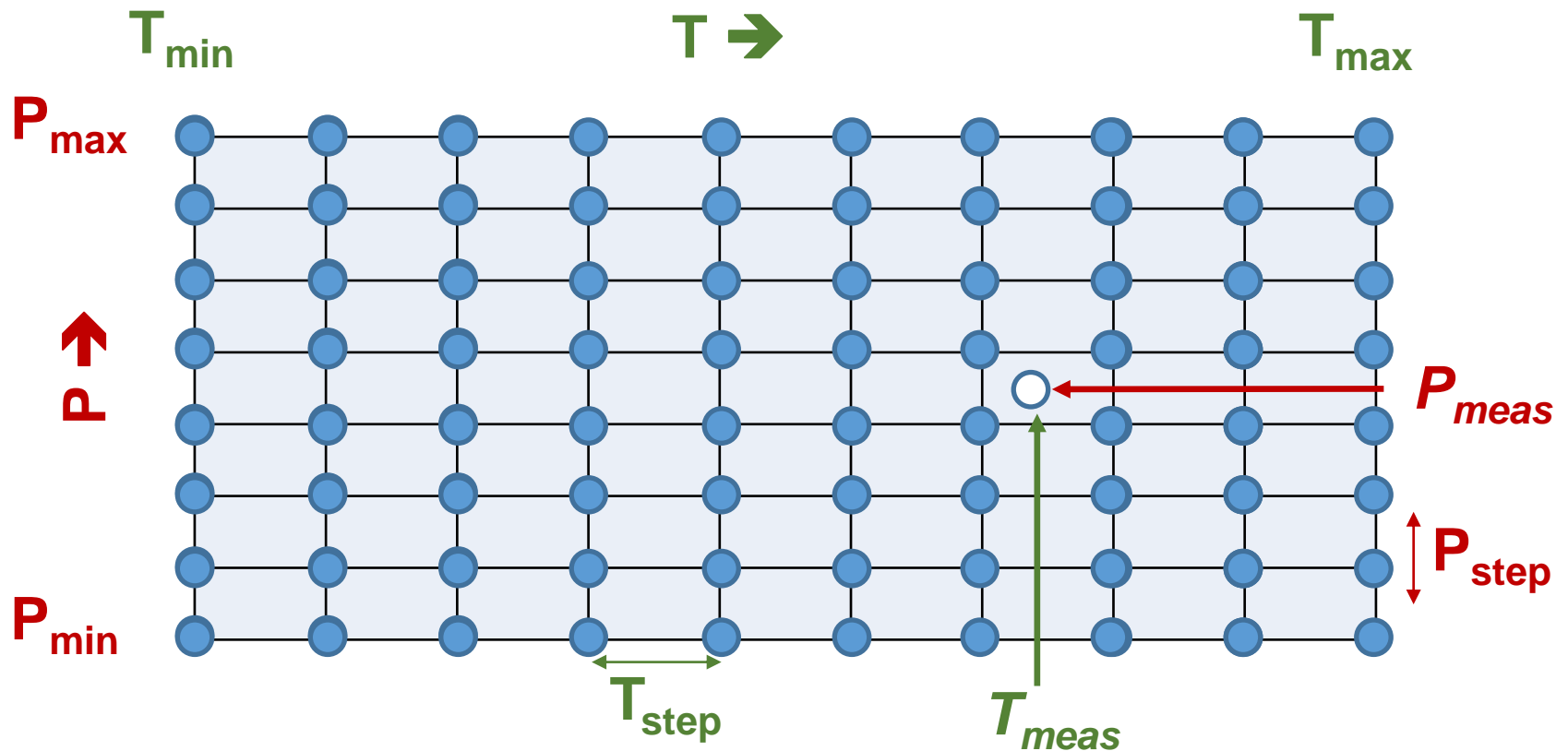
**(2) Calculate  $c_{\text{theo}}$  as a function of concentration from component  $C_p$ ,  $C_v$ 's over the expected sonar temperature, pressure range to make database of  $c_{\text{theo}}$  vs. *conc.* fit equations**

**(example here 0- 1%  $C_3F_8$  (m.w.= 188 in  $N_2$  (m.w.= 28): only one pressure shown here for clarity)**



(3) **CAN UTILITY:** Store these  $c_{\text{theo}}$  vs. molar conc. polyfit coeffs covering expected temperature & pressure range in “cans” at  $P, T$  grid intersections

(4) Calculate component concentrations  $\omega_i$  from *measured sound velocity*  $c_{\text{meas}}$  & stored fit coeffs. interpolated to correspond to the *measured*  $T, P$



!! This grid can become 3-D or higher-D with known contaminant gas(es) →



# Refractive index & GWP 'load' in a Cherenkov Gas Radiator

3 large RICH detectors currently in operation at CERN:  
using saturated fluorocarbon gas volumes ~ 50-100 m<sup>3</sup>:

C<sub>4</sub>F<sub>10</sub> (COMPASS, LHCb RICH 1):  $GWP_{20} = 4880$ ,

CF<sub>4</sub> (LHCb RICH 2):  $GWP_{20} = 6870$

A Cherenkov radiator vessel of volume  $V(m^3)$  filled with a blend of gases of densities  $\rho_i (kgm^{-3})$ , fractional concentrations  $w_i$  and individual  $GWP_i$  (tonnes CO<sub>2</sub> eq.) has a GWP environmental "load" (& release potential)  $L$  given by:

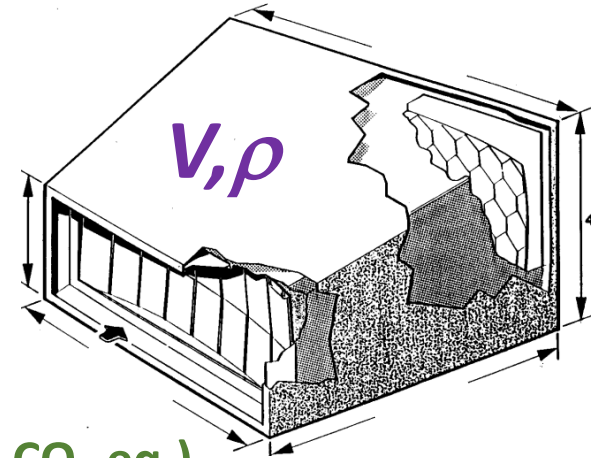
$$L = \frac{V}{1000} \sum_i (w_i \cdot \rho_i \cdot GWP_i) \quad (\text{tonnes CO}_2 \text{ eq.}) \quad [\text{Eq. (1)}]$$

The corresponding radiator gas mixture refractivity is given by :

$$(n-1)_{rad} = \sum_i (w_i \cdot (n-1)_i) \quad [\text{Eq. (2)}]$$

For just two gases we can blend small concentration  $\omega_x$  of (heavier) SFC or NOVEC<sup>®</sup> vapour of high refractivity  $(n-1)_x$  with  $\omega_y$  of light transparent gas, refractivity  $(n-1)_y$ , to replicate refractivity  $(n-1)_z$  of a lighter SFC at high conc. – for a lower GWP load.

$$\omega_x = \frac{(n-1)_z - (n-1)_y}{(n-1)_x - (n-1)_y} \quad [\text{Eq. (3)}]$$



Aah...but what if there are 3  
(or more) gases present?

## Acoustic Ambiguity ?

(2 or more combinations → same c...  
so find  $w_{3...}$  from different source...)

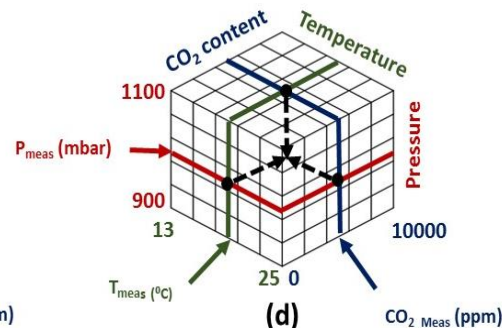
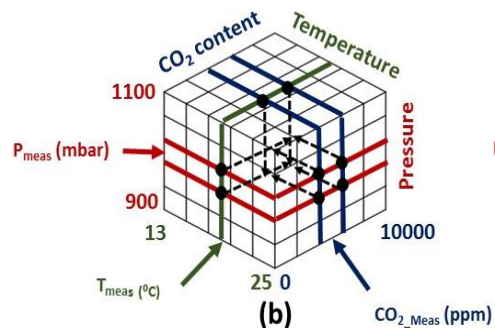
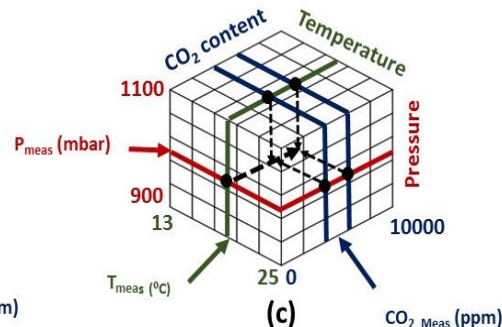
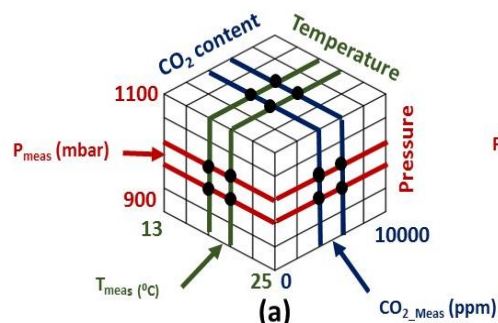
### Examples:

CO<sub>2</sub> from Non Dispersive IR,  
O<sub>2</sub> from Electrochemical cell,  
H<sub>2</sub>O from hygrometry... etc.

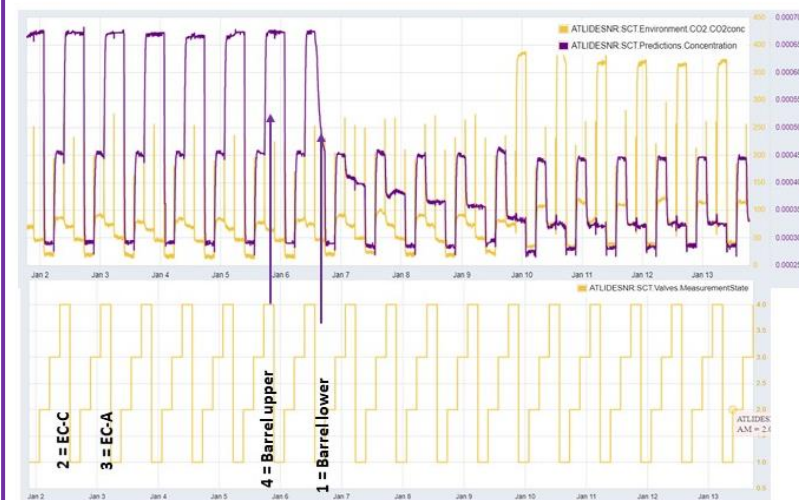
# Example: Look-up tables of SoS. vs. composition for $C_3F_8/N_2$ (+ $CO_2$ ) (ATLAS silicon tracker cooling leak analysis)

<https://www.mdpi.com/2410-390X/5/1/6>

Calculate **sound vel vs. conc. eqns** from  $C_3F_8$  &  $N_2$  AND KNOWN CONTAMINANT GAS  $C_p$  &  $C_v$  over expected  $T, P, \%CO_2$  range.



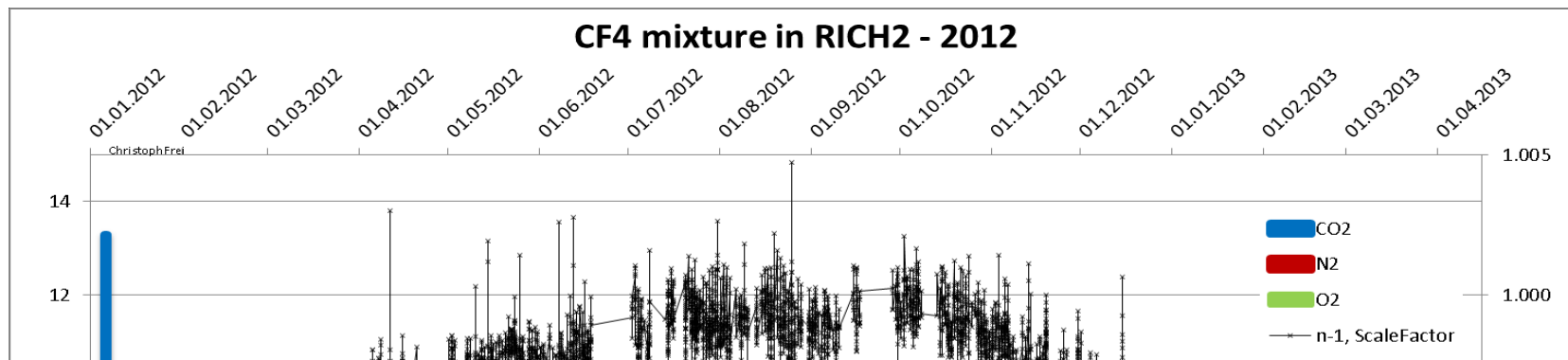
Drop in  $C_3F_8$  coolant contamination seen in SCT Barrel environmental volumes following SCT cooling shutdown Jan 6, 2020 (measured on top of varying  $CO_2$  contamination)



**Demonstration:**  
 1<sup>st</sup> acoustic measurement of concentrations of binary gas pair of interest ( $C_3F_8/N_2$ ) in known varying conc. of 3<sup>rd</sup> gas ( $CO_2$ ):  
 (4 envelopes cycling every 4 hours)  
 Algorithm: industrial & anaesthesia applications

LHCb RICH 2 radiator has **four** gases at significant (%-scale) concentration here illustration of change in refractivity with varying CO<sub>2</sub> concentration

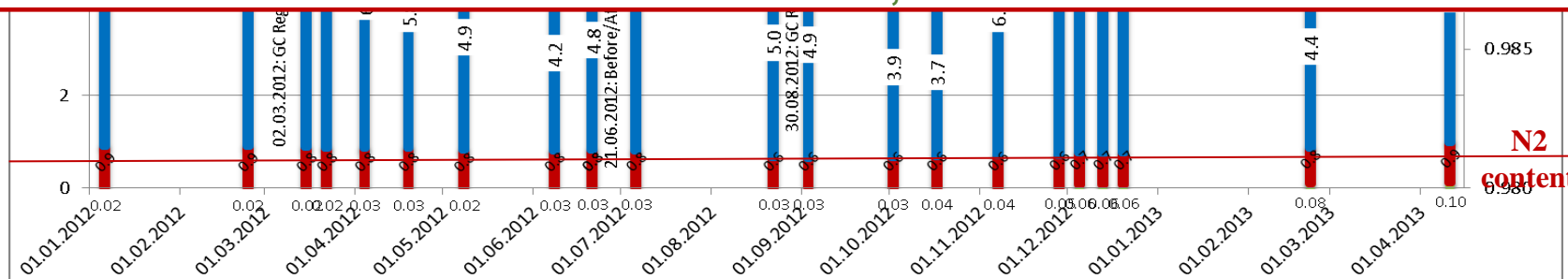
(From RICH2013)



CO<sub>2</sub> molar conc. measurement: NDIR:

O<sub>2</sub> molar conc. measurement: electrochemical fuel cell

N<sub>2</sub>/CF<sub>4</sub> molar conc. measurements best derived acoustically (on top of known O<sub>2</sub>, CO<sub>2</sub> conc.)



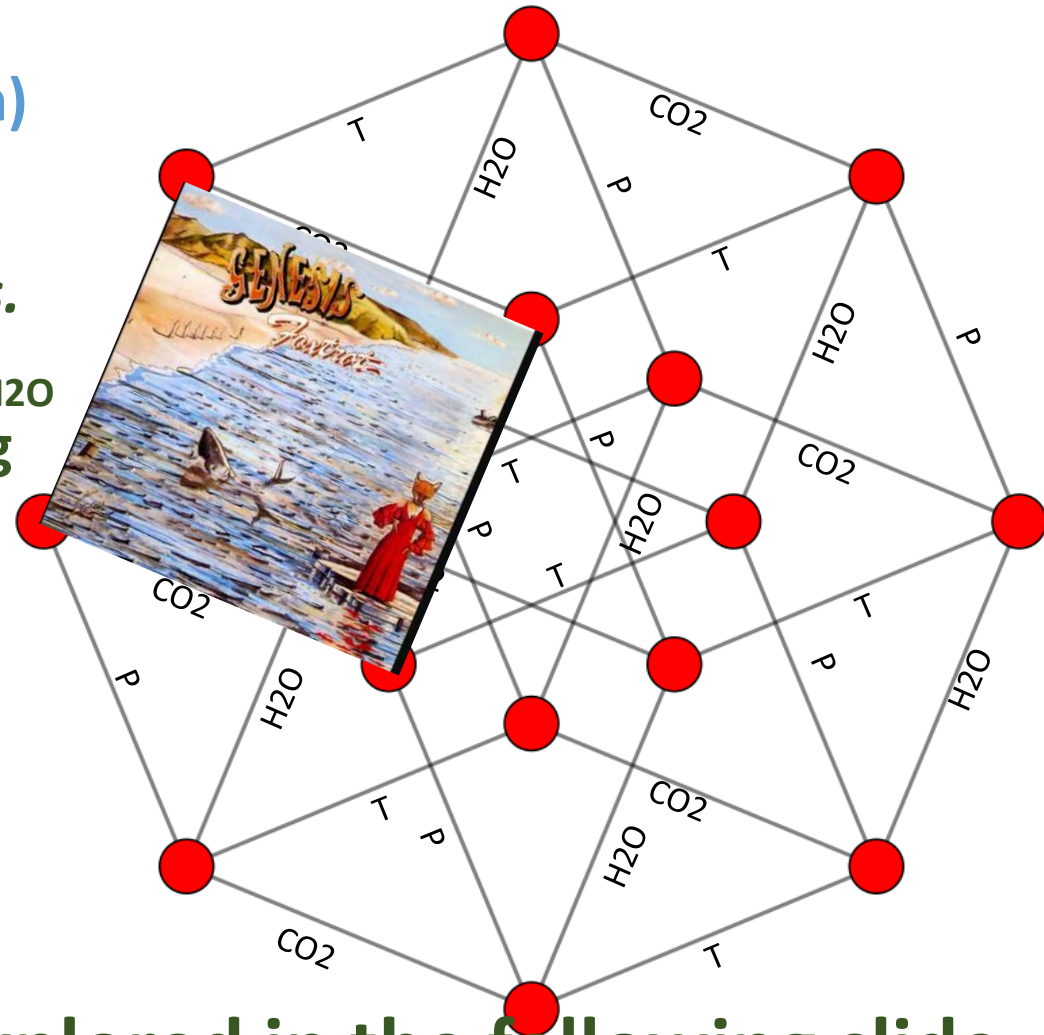
Example with a **second** known contaminant gas: here  $H_2O$  but could be another measurable gas like  $O_2$ : 4-D {T,P,  $CO_2$ ,  $H_2O$ } Process dataspace example 'Cans' of  $c$  vs.  $conc_{1,2}$  fit coefficients now at corners of tesseract.

(Here in Coxeter B4 projection)

“Can Utility”:

Fit parameters to sound vel vs. conc  $C_5F_{10}O/N_2$  @ T, P,  $\omega_{O_2}$ ,  $\omega_{H_2O}$  stored in nearest cans forming corners of 2 cubes in a Tesseract (T has 8 cube faces)

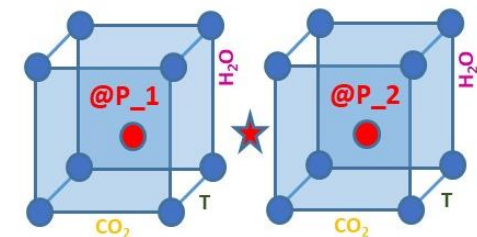
- 2 x {T,P, $CO_2$ } exc.  $H_2O$
- 2 x {T,P,  $H_2O$ } exc.  $CO_2$
- 2 x {T,  $CO_2$ ,  $H_2O$ } exc. P
- 2 x {P,  $CO_2$ ,  $H_2O$ } exc. T



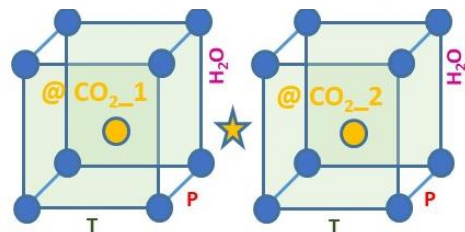
Opposite cubic faces explored in the following slide



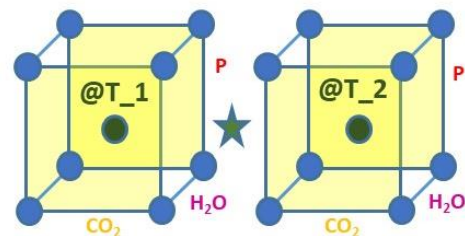
# Extractio-reduction



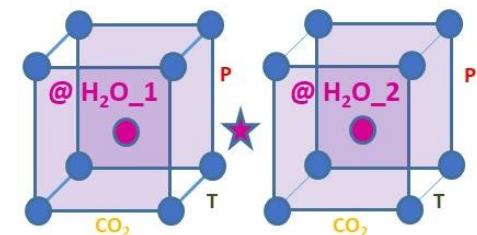
(a)  $@P_1 \rightarrow P_{meas} \leftarrow @P_2$



(b)  $@CO_{2_1} \rightarrow CO_{2\_meas} \leftarrow @CO_{2_2}$

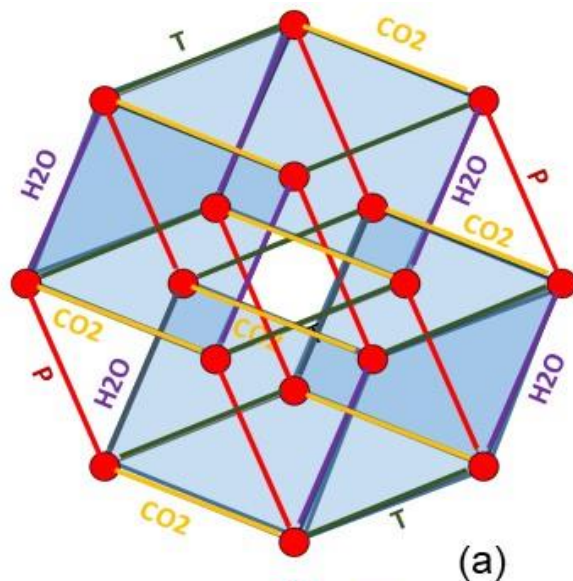


(c)  $@T_1 \rightarrow T_{meas} \leftarrow @T_2$

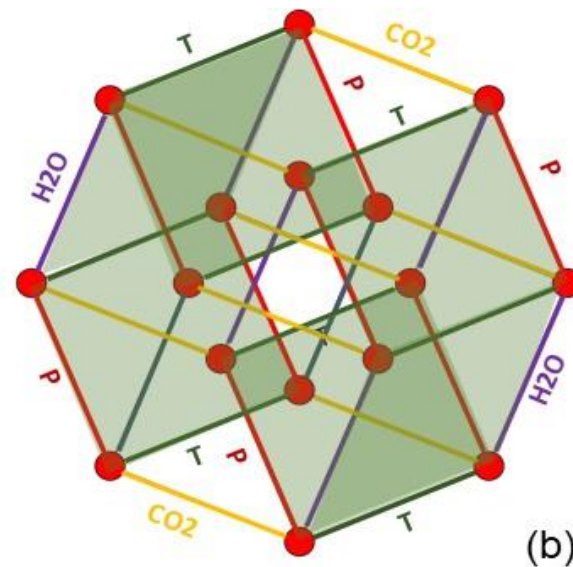


(d)  $@H_{2O_1} \rightarrow H_{2O\_meas} \leftarrow @H_{2O_2}$

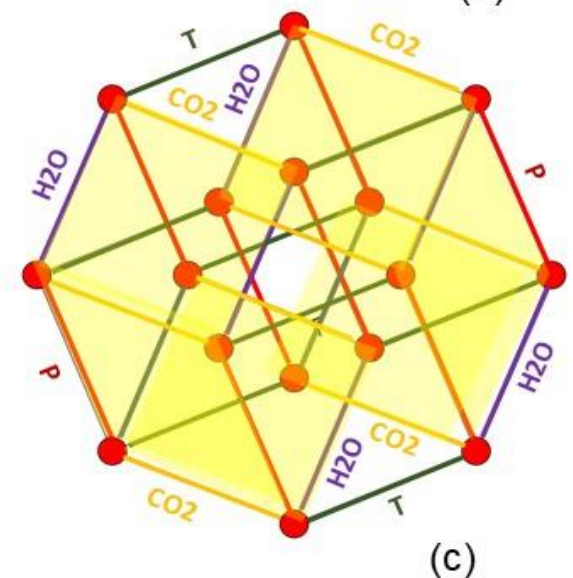
# Tessar-Action



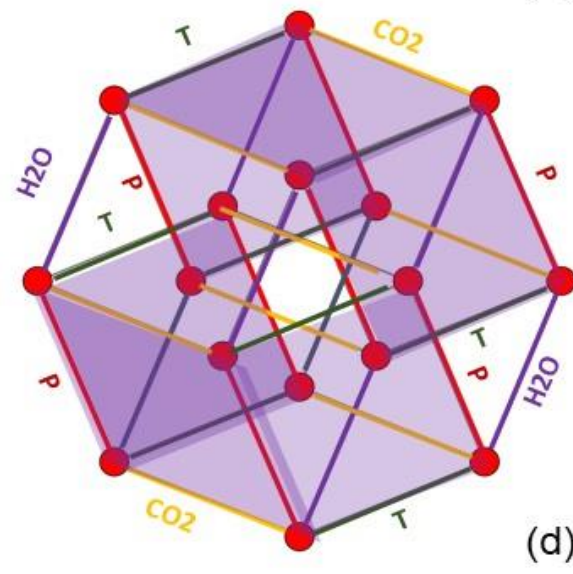
(a)



(b)



(c)



(d)

<https://www.mdpi.com/2410-390X/5/1/6>

# Database growth control

(important in instruments using embedded  $\mu$ -controllers)

**CAN FILLING:** Of course,  $C_p$  &  $C_v$  for all gases (primary & background) must be calculated for all T, P points on the  $n$ -D grid;

**CAN UTILITY:** Calculate & fit  $c$  in gas pair of primary interest from  $C_p$  &  $C_v$  over their conc. range AND @T, P, known background gas conc. Grid points.

Database size (3-D example)

$$DB\ size = No.\ primary\ fit\ coeffs * \frac{RoI\_T}{d\_T} * \frac{RoI\_P}{d\_P} * \frac{RoI\_Conc.bkd\ gas\ 1}{d\_Conc.bkd\ gas\ 1} \dots$$

*RoI<sub>n</sub> = range of interest<sub>n</sub>; d<sub>n</sub> = stepsize<sub>n</sub> → Database explosion !?!*

- Increasing stepsize (→ longer interpolation distance) can reduce No. of cans (“cubes” become “cuboids”)...
- *Some dimensions can be suppressed altogether using physical law (rather than empirical changes):*
- *example for temperature dimension:*  $c_{t_{abs1}} = c_{t_{abs0}} \sqrt{\frac{t_{abs1}}{t_{abs0}}}$



LHCb RICH 2 radiator has **four** gases at significant (%-scale) concentration  
 here illustration of change in refractivity with varying CO<sub>2</sub> concentration

(From RICH2013)

**CO<sub>2</sub> molar conc. measurement: NDIR:**

**O<sub>2</sub> molar conc. measurement: electrochemical fuel cell**

**N<sub>2</sub> CF<sub>4</sub> molar conc. measurements best derived acoustically  
 (on top of known O<sub>2</sub>, CO<sub>2</sub> conc.)**

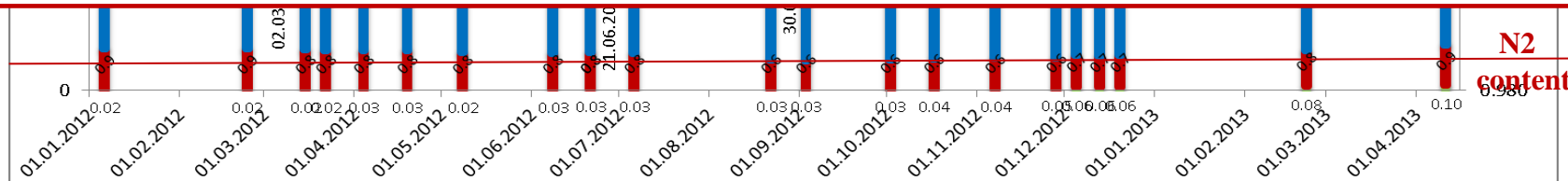
$$N_2(n-1)_{(y)} = 300.10^{-6}, \quad CO_2(n-1)_{(j1)} = 450.10^{-6}, \quad O_2(n-1)_{(j2)} = 250.10^{-6}$$

$$(CF_4(n-1)_{(target)} = 488.10^{-6})$$

**Possible NOVEC5110 C<sub>5</sub>F<sub>10</sub>O/N<sub>2</sub> (or C<sub>5</sub>F<sub>10</sub>O/CO<sub>2</sub>)**

$$C_5F_{10}O(n-1)_{(x)} \sim 1750.10^{-6}$$

**substitution would have a big GWP advantage...**



# Extension to a Cherenkov Gas Radiator with extra **known** (= measured) concentrations of background gases (eg LHCb RICH 2: **CF<sub>4</sub>**, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>)

$$CF_4 \text{ GWP}_{20} = 6870 \text{ Target refractivity} = (n-1)_z = 488.10^{-6}$$

From previous slide, the radiator gas mixture overall refractivity is given by :

$$(n-1)_{rad} = \sum_{i=1}^{i_{max}} (w_i \cdot (n-1)_i) \text{ where } i \text{ is the set of ALL gases present}$$

When *j* **contaminant gases** of known molar concentrations  $w_j$  are present we can still blend a small concentration  $\omega_x$  of (heavier) SFC or NOVEC® vapour of high refractivity  $(n-1)_x$  with  $\omega_y$  of light transparent gas to substitute the refractivity  $(n-1)_z$  of a lighter SFC at high concentration – to achieve a **lower overall GWP load**.

$$(n-1)_{z(target)} = w_x [(n-1)_x - (n-1)_y] + (n-1)_y + \sum_{j=1}^{j_{max}} w_j [(n-1)_j - (n-1)_y] \quad [\text{Eq. (2)} \rightarrow \text{Eq. (2b)}]$$

$$\omega_x = \frac{(n-1)_z - (n-1)_y + \sum_{j=1}^{j_{max}} w_j [(n-1)_y - (n-1)_j]}{(n-1)_x - (n-1)_y} \quad [\text{Eq. (3)} \rightarrow \text{Eq. (3b)}]$$

# On the turning away...

## The uncertain ECHA path to prohibition (a 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>

**Need to clarify 3M and other manufacturers'  
attitudes to future fluoroketone (C<sub>n</sub>F<sub>2n</sub>O) production  
Electronics industry is the driver!**

# Conclusion

**Saturated ( $C_nF_{(2n+2)}$ ) fluorocarbons** under attack for their high GWP

- Reduce wastage, purification loss in present installations;
- Mix smaller molar concentrations of heavy SFCs  
or better  $C_nF_{2n}O$  with light  $N_2$  etc. carriers for desired ref. index;

**SLAC SLD CRID sonar (1990s): demonstrated Cherenkov angle/ $\beta$  measurement & dynamic  $C_5F_{12}/N_2$  blend control: ultrasonic feedback to flow controllers**

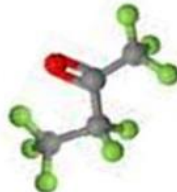
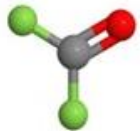
Refractive index can be continuously monitored by ultrasound even in dynamically-varying multi-mixes, if 3<sup>rd</sup>,4<sup>th</sup>.. component concs. known from other sensors ;

**New (non-cyclic)  $C_nF_{2n}O$  molecules very promising (particularly  $C_5F_{10}O$  (3M NOVEC ® 5110)):** blend studies starting (Antonello Di Mauro) (need optical, desiccation, thermodynamic (circulation) studies) → potentially huge GWP savings

→  $CF_2O$  & *lin.*  $C_4F_8O$  would be ideal...

***We are a small-scale users who will always ride on the coat-tails for the semiconductor manufacturing industry.***

**We should nonetheless enter discussions with manufacturers!**



# References and back-up material

## Cherenkov radiator and related general references (1 of 2) from

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

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- [2] B. Mandelli; Eco-gas mixtures and mitigation procedures for Green-house Gases (GHGs); ECFA Detector R&D Road-map Symposium: T.F. 1 Gaseous Detectors, 29/4/2021  
[https://indico.cern.ch/event/999799/contributions/4204191/attachments/2236047/3789965/BMandelli\\_ECFA.pdf](https://indico.cern.ch/event/999799/contributions/4204191/attachments/2236047/3789965/BMandelli_ECFA.pdf),
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[https://indico.cern.ch/event/1094055/contributions/4932286/attachments/2508724/4311387/RICH2022\\_C4F10\\_dallatorre.pdf](https://indico.cern.ch/event/1094055/contributions/4932286/attachments/2508724/4311387/RICH2022_C4F10_dallatorre.pdf)
- [6] 3M PFG-3480: c-octofluorotetrahydrofuran (C<sub>4</sub>F<sub>8</sub>O). **Note:** fluid out of production : product reference now used for a non-fluidic product. For historic product data sheet mentioning its high GWP see (for example):  
[http://static6.arrow.com/aropdfconversion/a7116f41dfdd5b79d2eb7b40afd687f8af23d8ef/mediawebserver\(563\).pdf](http://static6.arrow.com/aropdfconversion/a7116f41dfdd5b79d2eb7b40afd687f8af23d8ef/mediawebserver(563).pdf)
- [7] M. Artuso et al; [Nucl. Instr & Meth. A Volume 558, \(2006\), 373-387](#)
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<https://multimedia.3m.com/mws/media/124688O/3m-novec-1230-fire-protection-fluid.pdf>
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3M Performance Materials 3M Center, St. Paul, MN 55144



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S. Easo; LHCb-RICH detectors and their gas radiators

<https://indico.cern.ch/event/1022051/contributions/4333562/attachments/2231064/3780374/LHCb-RICH-Current-GasRadiators-April-2021.pdf>,

Options for alternate radiators in LHCb-RICH system (including calculations by O. Ullaland); S. Easo,

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<https://echa.europa.eu/hot-topics/perfluoroalkyl-chemicals-pfas>

← → ↻ <https://echa.europa.eu/-/echa-publishes-pfas-restriction-proposal> 67% ☆

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### 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.

← → ↻ <https://echa.europa.eu/candidate-list-table> 67% ☆

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EUROPEAN CHEMICALS AGENCY

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## 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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**ECHA**  
EUROPEAN CHEMICALS AGENCY

**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:**

**BAuA**  
Federal Institute for Occupational Safety and Health  
Division 5 - Federal Office for Chemicals  
Friedrich-Henkel-Weg 1-25  
D-44149 Dortmund, Germany

**Bureau REACH, National Institute for Public Health and the Environment (RIVM)**  
Antonie van Leeuwenhoeklaan 9  
3721 MA Bilthoven, The Netherlands

**Swedish Chemicals Agency (KEMI)**  
PO Box 2,  
SE-172 13 Sundbyberg, Sweden

**Norwegian Environment Agency**  
P.O. Box 5672 Torgarden  
N-7485 Trondheim, Norway

**The Danish Environmental Protection Agency**  
Tolderundsvej 5  
5000 Odense C, Denmark

**VERSION NUMBER:** 2  
**DATE:** 22.03.2023

P.O. Box 400, FI-00121 Helsinki, Finland | Tel. +358 9 686180 | Fax +358 9 68618210 | [echa.europa.eu](https://echa.europa.eu)

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## Latest updates

### Broad PFAS restriction proposal:

- First Q&As published from the info session, 3 May 2023
- Watch the info session on the proposed PFAS restriction
- Have your say on the proposal to restrict PFAS by 25 September 2023
  - Direct link to consultation
- ECHA publishes PFAS restriction proposal, 7 February 2023
  - Recording of media briefing held by the five national authorities

### Restriction proposal on PFASs in firefighting foams:

- ECHA's scientific committees take more time to conclude on restricting PFASs in firefighting foams, 19 Oct 2022
- Proposal to ban 'forever chemicals' in firefighting foams throughout the EU, 23 Feb 2022

### Other:

- Perfluoroheptanoic acid (PFHpA) and its salts added to Candidate List of substances of very high concern, 17 January 2023

REPORT

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ision and EU

en Deal:  
proposes rules for  
d water, 26 Oct

ally adopts further  
'forever chemicals'  
Oct 2022  
ategy for

Some Conclusions at this stage : drawing on

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

- **Is the banning of all fluorocarbons...a realistic aim? ... probably not...**
- **3M seem to have lost enthusiasm to produce fluorinated fluids after 2025, but companies like F2 Chemicals (Preston, UK), **Astor (Ru)**, Synquest (FL), Techspray (GA) continue (probably many others: e.g.China): **groups at CERN looking into alternative suppliers (stated Jan 26 2024)****
- ***We are a small-scale users who will always ride on the back of the semiconductor industry.***
- ***We should nonetheless enter discussions with other manufacturers!***  
***CERN is already doing this!***

***But*** discussion should concentrate on  $C_nF_{2n}O$  molecules over the full carbon spectrum with GWP = 0.



CERN  
CH1211 Geneva 23  
Switzerland

EN Engineering Department

EDMS NO. <b>1751219</b>	REV. <b>1.0</b>	VALIDITY <b>Released</b>
REFERENCE <b>2017-334</b>		

Date: 2017-12-22

## Technical Note

### NOVEC Fluids Qualification Report

**NOVEC 649: C<sub>6</sub>F<sub>12</sub>O: GWP <1**  
**NOVEC 7100: C<sub>5</sub>F<sub>9</sub>H<sub>3</sub>O: GWP = 297**

**Report on the study executed for the qualification of the NOVEC Fluid for Detector Cooling applications**

DOCUMENT PREPARED BY: Javier Quinones – CIEMAT Marta Fernandez – CIEMAT Petr Gorbounov – EP-UAT Dina Giakoumi – EP-DT Radu Setnescu - ICPE-CA Marius Lungulescu - ICPE-CA	DOCUMENT CHECKED BY: Mauro Taborelli - TE-VSC Benoit Teissandier - TE-VSC	DOCUMENT APPROVED BY: Michele Battistin - EN-CV
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Taking into account the results of the analysis described above, the project suggests the use of N649 as a replacement of C<sub>6</sub>F<sub>14</sub> for detector cooling applications. The following table summarizes qualitatively the parameters of the selection.

	N649	N7100	"C <sub>6</sub> F <sub>14</sub> " (Flutec PP1)
GWP	I	II	III
Radiation induced destruction rate	I	I	I
PFIB production under irradiation	II	III	suspected production
Hydrolysis	II	I	I
Molecular Sieves compatibility	I	I	I
Activated Carbon efficiency	I	I	I
Acidity increase /10 kGy	II	III	I
[F ] Increase /10 kGy)	II	III	I

#### Open issues

There are currently two ongoing tests, additional to those mentioned in this report. The compatibility testing of materials with Novec 649 and the testing of Novec 649 on a test bench. Their results will be shortly published on a second version of this report.

Additionally, the following points have not been fully investigated in the frame of this project and could be part of a future development:

- On-line moisture content monitoring sensors
- Acid removal from the Novec cooling systems
- Temperature dependence of the Novec 649 hydrolysis rate

#### Summary

Both studied NOVEC fluids have their initial (as received) purity in conformity with the CERN minimal purity requirement for C<sub>6</sub>F<sub>14</sub>. In terms of the radiolytic destruction rate determined up to the gamma dose of 100 kGy, they turned out to have the radiation resistance comparable with that of C<sub>6</sub>F<sub>14</sub>.

After the analysis of both Novec fluids, N649 is suggested to replace C<sub>6</sub>F<sub>14</sub> for detector cooling applications with coolant dose up to 100 kGy.

Toxic radiolysis products, including hydrolysable fluoride compounds (e.g. COF<sub>2</sub>) and even the highly toxic PFIB, were detected in both fluids and turned out to be significantly more abundant in N7100. AC filters were experimentally tested and proved to be efficient for the elimination of toxic radiolysis products, apart from PFIB. It was impossible to test PFIB removal mainly due to the unavailability of reference samples. However, 3M detected very low values of PFIB and reported that, in the case of a typical spill of N649 irradiated to 100 kGy, without any filtering, the dilution in the air could cause at most mild, transient health effects after one hour of continuous inhalation.



REFERENCE <b>2017-334</b>	EDMS NO. <b>1751219</b>	REV. <b>1.0</b>	VALIDITY <b>Released</b>
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In C<sub>6</sub>F<sub>14</sub>-based systems at CERN, molecular sieves were traditionally used as desiccants to drive the moisture content to very low levels required for operation. The same drying agents were tested with N649 and proved to be efficient, without any indications of reactivity.

A 2nd version of the report concerning the compatibility with materials will follow.

**NOVEC 649 cools MAPMTs in LHCb!**



---

# Studies to reduce greenhouse gas emissions from detectors at the LHC

<https://indico.cern.ch/event/1155238/attachments/2436920/4173752/EP-DT%20Seminar%20May%202022.pdf>

Gianluca Rigoletti

EP-DT Seminar, 04/05/2022



EP-DT  
Detector Technologies

## Options for alternate radiators for LHCb-RICH system

*CERN: Mini-Workshop on gas transport parameters  
for present and future generation of experiments*



On behalf of LHCb-RICH group

<https://indico.cern.ch/event/1022051/contributions/4319538/attachments/2231436/3781060/LHCb-RICH-Future-Radiators.pdf>

S.Easo  
22-04-2021



IPCC data sources for more information:

- AR4 values: [https://www.ipcc.ch/publications\\_and\\_data/ar4/wg1/en/ch2s2-10-2.html](https://www.ipcc.ch/publications_and_data/ar4/wg1/en/ch2s2-10-2.html)
- AR5 values: [https://www.ipcc.ch/pdf/assessment-report/ar5/wg1/WG1AR5\\_Chapter08\\_FINAL.pdf](https://www.ipcc.ch/pdf/assessment-report/ar5/wg1/WG1AR5_Chapter08_FINAL.pdf) (p. 73-79)

## Global Warming Potential Values

The following table includes the 100-year time horizon global warming potentials (GWP) relative to CO<sub>2</sub>. This table is adapted from the IPCC Fifth Assessment Report, 2014 (AR5)<sup>i</sup>. The AR5 values are the most recent, but the second assessment report (1995) and fourth assessment report (2007) values are also listed because they are sometimes used for inventory and reporting purposes. For more information, please see the IPCC website ([www.ipcc.ch](http://www.ipcc.ch)). The use of the latest (AR5) values is recommended. Please note that the GWP values provided here from the AR5 for non-CO<sub>2</sub> gases do not include climate-carbon feedbacks.

**Global warming potential (GWP) values relative to CO<sub>2</sub>**

<sup>i</sup> Myhre, G., D. Shindell, F.-M. Bréon, W. Collins, J. Fuglestedt, J. Huang, D. Koch, J.-F. Lamarque, D. Lee, B. Mendoza, T. Nakajima, A. Robock, G. Stephens, T. Takemura and H. Zhang, 2013: Anthropogenic and Natural Radiative Forcing. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

	Chemical formula	GWP values for 100-year time horizon		
		Second assessment report (SAR)	Fourth Assessment Report (AR4)	Fifth Assessment Report (AR5)
<b>Perfluorinated compounds</b>				
Sulfur hexafluoride	SF <sub>6</sub>	23,900	22,800	23,500
Nitrogen trifluoride	NF <sub>3</sub>		17,200	16,100
PFC-14	CF <sub>4</sub>	6,500	7,390	6,630
PFC-116	C <sub>2</sub> F <sub>6</sub>	9,200	12,200	11,100
PFC-218	C <sub>3</sub> F <sub>8</sub>	7,000	8,830	8,900
PFC-318	c-C <sub>4</sub> F <sub>8</sub>	8,700	10,300	9,540
PFC-31-10	C <sub>4</sub> F <sub>10</sub>	7,000	8,860	9,200
PFC-41-12	C <sub>5</sub> F <sub>12</sub>	7,500	9,160	8,550
PFC-51-14	C <sub>6</sub> F <sub>14</sub>	7,400	9,300	7,910
PCF-91-18	C <sub>10</sub> F <sub>18</sub>		>7,500	7,190
Trifluoromethyl sulfur pentafluoride	SF <sub>5</sub> CF <sub>3</sub>		17,700	17,400
Perfluorocyclopropane	c-C <sub>3</sub> F <sub>6</sub>			9,200

**Pressure-enthalpy plots for various  
Saturated fluorocarbons and blends  
(Circulation thermodynamics)**

# SLD Barrel CRID $C_5F_{12}/N_2$ gas radiator: continuous thermodynamic recirculation

SLAC-PUB-5988  
October 1992  
(1)

## THE FLUID SYSTEMS FOR THE SLD CHERENKOV RING IMAGING DETECTOR\*

K. Abe,<sup>a</sup> P. Antilogus,<sup>b,i</sup> D. Aston,<sup>b</sup> K. Baird,<sup>c</sup> A. Bean,<sup>d</sup> R. Ben-David,<sup>e</sup> T. Bienz,<sup>b,iii</sup>  
F. Bird,<sup>b,iii</sup> D. O. Caldwell,<sup>d</sup> M. Cavalli-Sforza,<sup>f</sup> J. Coller,<sup>g</sup> P. Coyle,<sup>f,iv</sup> D. Coyne,<sup>f</sup>  
S. Dasu,<sup>b,v</sup> S. Dolinsky,<sup>b,vi</sup> A. d'Oliveira,<sup>b,vii</sup> J. Duboscq,<sup>d,viii</sup> W. Dunwoodie,<sup>b</sup> P. Gagnon,<sup>f</sup>  
G. Hallewell,<sup>b,iv</sup> K. Hasegawa,<sup>g</sup> Y. Hasegawa,<sup>g</sup> J. Huber,<sup>d,ix</sup> Y. Iwasaki,<sup>g</sup> P. Jacques<sup>c</sup>  
R. A. Johnson,<sup>h</sup> M. Kalelkar,<sup>c</sup> H. Kawahara,<sup>b,10</sup> Y. Kwon,<sup>b</sup> D. W. G. S. Leith,<sup>b</sup> X. Liu,<sup>f</sup> A. Lu,<sup>d</sup>  
S. Manly,<sup>e</sup> J. Martinez,<sup>h</sup> L. Mathys,<sup>d,x</sup> M. McCulloch,<sup>b</sup> S. McHugh,<sup>d</sup> D. McShurley,<sup>b</sup> G. Müller,<sup>b</sup>  
D. Muller,<sup>b</sup> T. Nagamine,<sup>b</sup> M. Nussbaum,<sup>h</sup> T. J. Pavel,<sup>b</sup> H. Peterson,<sup>b</sup> R. Plano,<sup>c</sup> B. Ratcliff,<sup>b</sup>  
R. Reif,<sup>b</sup> P. Rensing,<sup>h</sup> A. K. S. Santha,<sup>h</sup> M. Schneider,<sup>f</sup> D. Schultz,<sup>b</sup> J. T. Shank,<sup>g</sup> S. Shapiro,<sup>b</sup>  
H. Shaw,<sup>b</sup> C. Simopoulos,<sup>b</sup> J. Snyder,<sup>e</sup> M. D. Sokoloff,<sup>h</sup> E. Solodov,<sup>b,xi</sup> P. Stamer,<sup>g</sup> I. Stockdale,<sup>h,xi</sup>  
F. Suekane,<sup>g</sup> N. Toge,<sup>b,xii</sup> J. Turk,<sup>g</sup> J. Va'vra,<sup>g</sup> R. Watt,<sup>b</sup> T. Weber,<sup>b</sup> J. S. Whitaker,<sup>g</sup>  
D. A. Williams,<sup>f</sup> S. H. Williams,<sup>b</sup> R. J. Wilson,<sup>f</sup> G. Word,<sup>c</sup> S. Yellin,<sup>d</sup> H. Yuta<sup>a</sup>

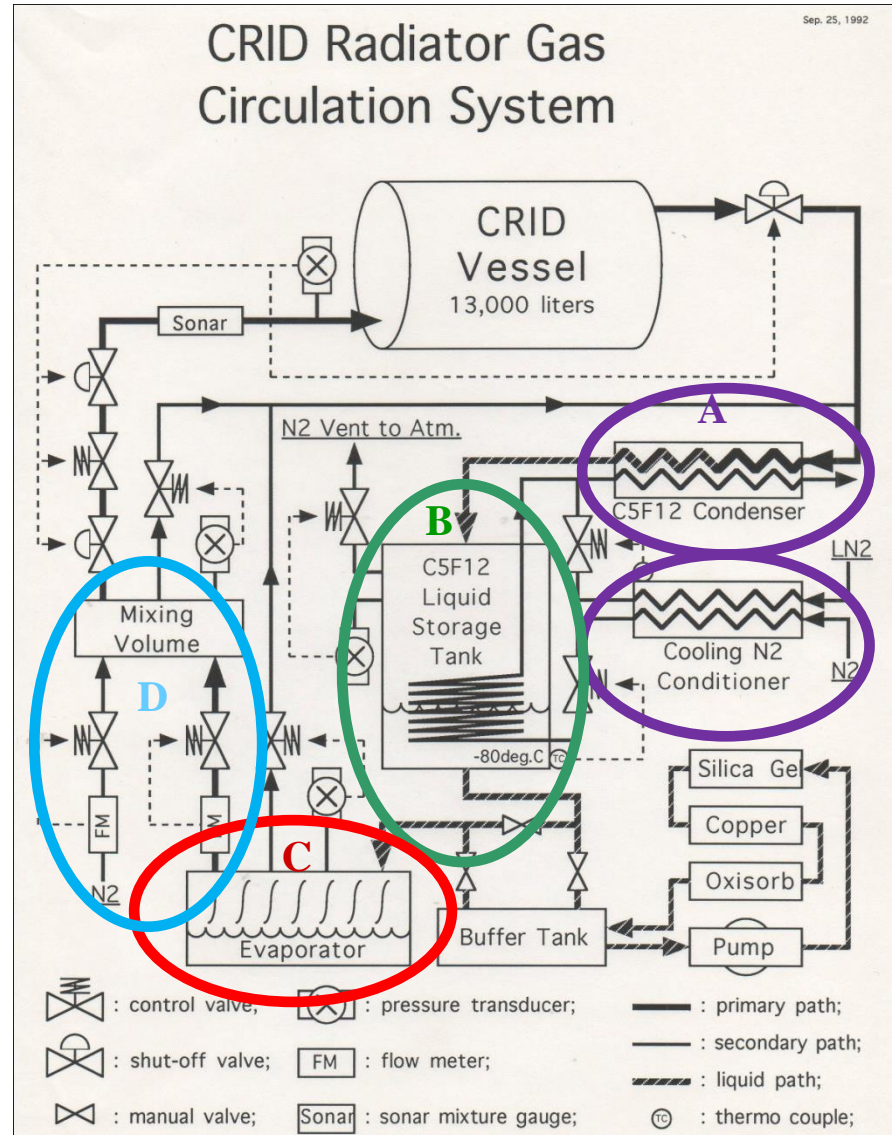
Low temperature (-80°C)

$N_2$  gas-induced condensation (B):  
of  $C_5F_{12}$  from  $C_5F_{12}/N_2$  radiator gas  
(flow ~1m<sup>3</sup>/hr, negligible  $C_5F_{12}$  loss)

followed by (C) electric re-evaporation  
(1-1.5m below condenser liq. level)

Cold  $N_2$  gas ('conditioned' by  
counter-flow with boil-off LN<sub>2</sub>  
from liquid argon calorimeter: (A))

Ultrasonic (speed of sound) – aided  
“on-the fly” mixing of typical  
17% $N_2$  /83% $C_5F_{12}$  (molar) radiator  
gas mixture (D)





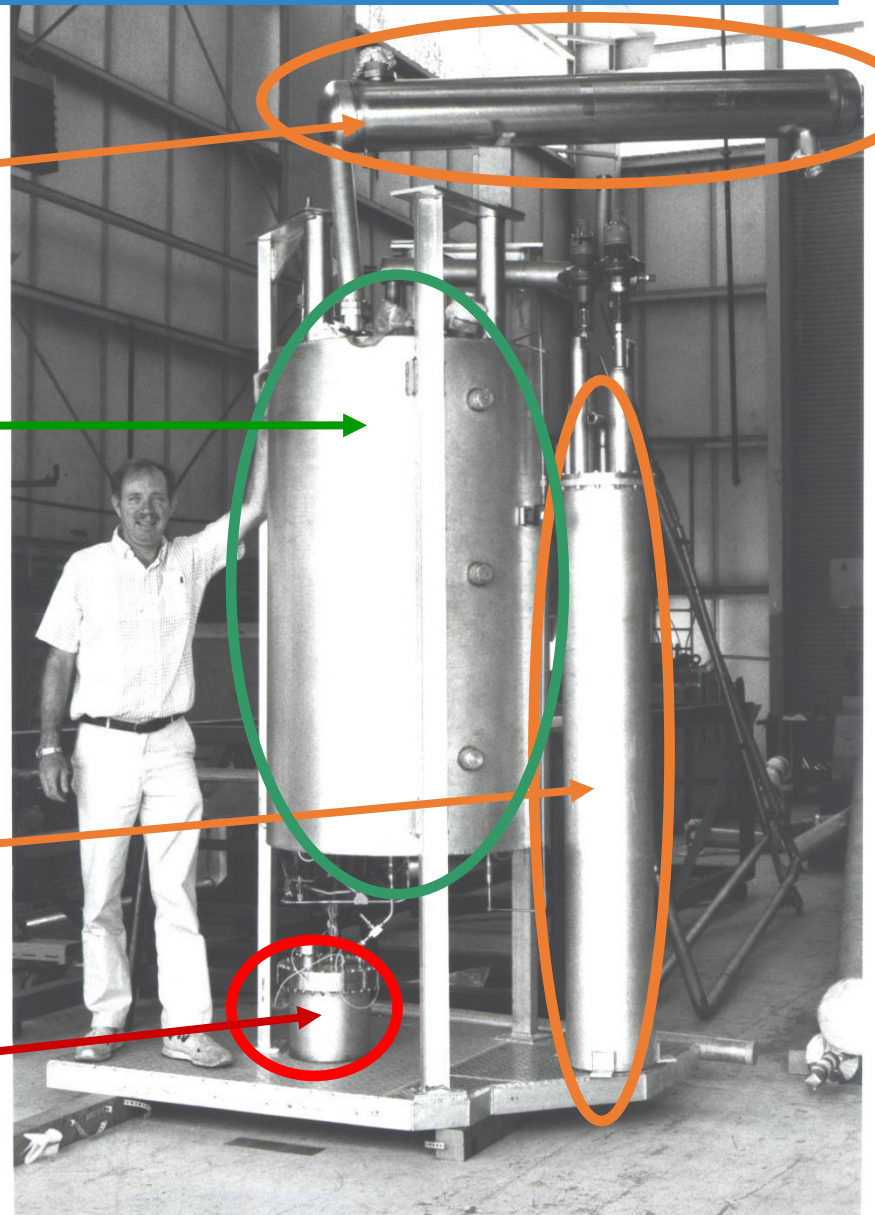
# SLD Barrel CRID $C_5F_{12}/N_2$ gas thermodynamic recirculator

(A)  $C_5F_{12}$  Condenser  
(cooled with  $GN_2$ )

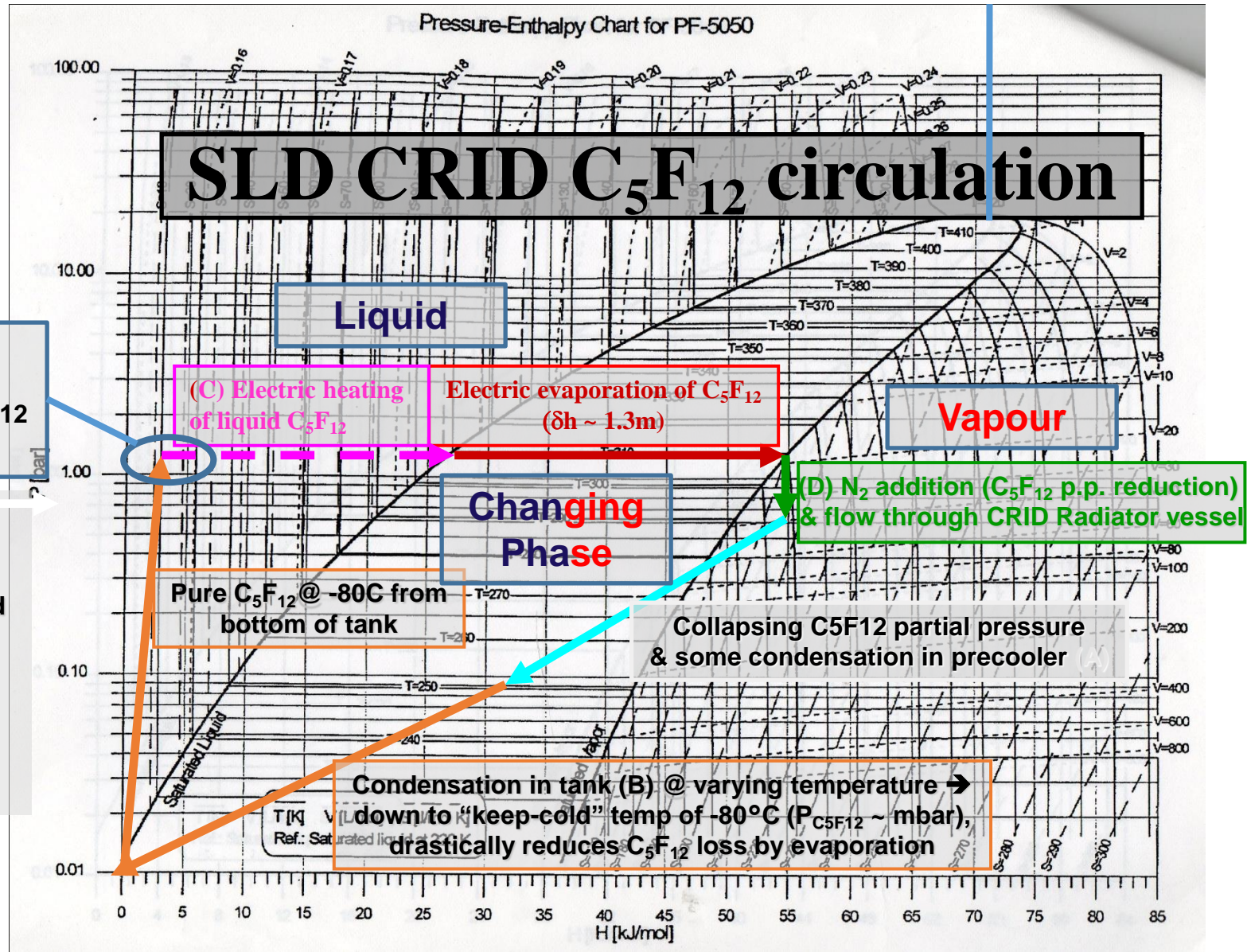
(B)  $C_5F_{12}$  storage tank  
and  $N_2$  separator

$LN_2$  conditioner  
(Chills  $GN_2$  in counterflow with  $LN_2$   
from liquid argon calorimeter source)

(C)  $C_5F_{12}$  Evaporator



**SLD CRID C<sub>5</sub>F<sub>12</sub> Thermodynamic circulation: Pressure-Enthalpy**



$\rho gh$  of 1.5m C<sub>5</sub>F<sub>12</sub>

1bar<sub>abs</sub> condenser Headspace (& CRID radiator vessel) pressure maintained by N<sub>2</sub> in return radiator gas & condenser N<sub>2</sub> vent to atmosphere

**SLD CRID C<sub>5</sub>F<sub>12</sub> circulation**

Liquid

Vapour

Changing Phase

Pure C<sub>5</sub>F<sub>12</sub> @ -80C from bottom of tank

Condensation in tank (B) @ varying temperature down to "keep-cold" temp of -80°C (P<sub>C<sub>5</sub>F<sub>12</sub></sub> ~ mbar), drastically reduces C<sub>5</sub>F<sub>12</sub> loss by evaporation

(C) Electric heating of liquid C<sub>5</sub>F<sub>12</sub>

Electric evaporation of C<sub>5</sub>F<sub>12</sub> ( $\delta h \sim 1.3m$ )

(D) N<sub>2</sub> addition (C<sub>5</sub>F<sub>12</sub> p.p. reduction) & flow through CRID Radiator vessel

Collapsing C<sub>5</sub>F<sub>12</sub> partial pressure & some condensation in pre-cooler

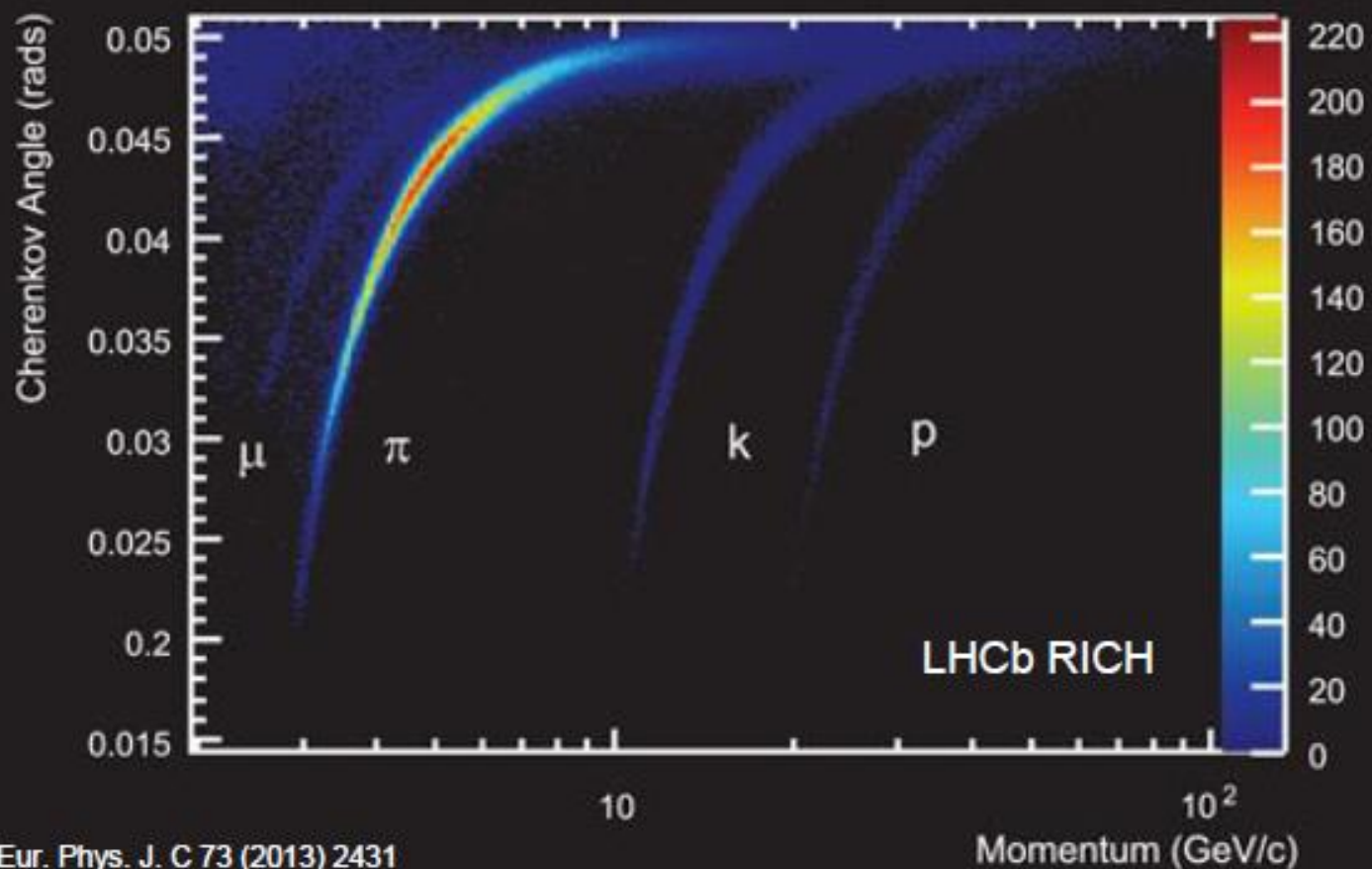


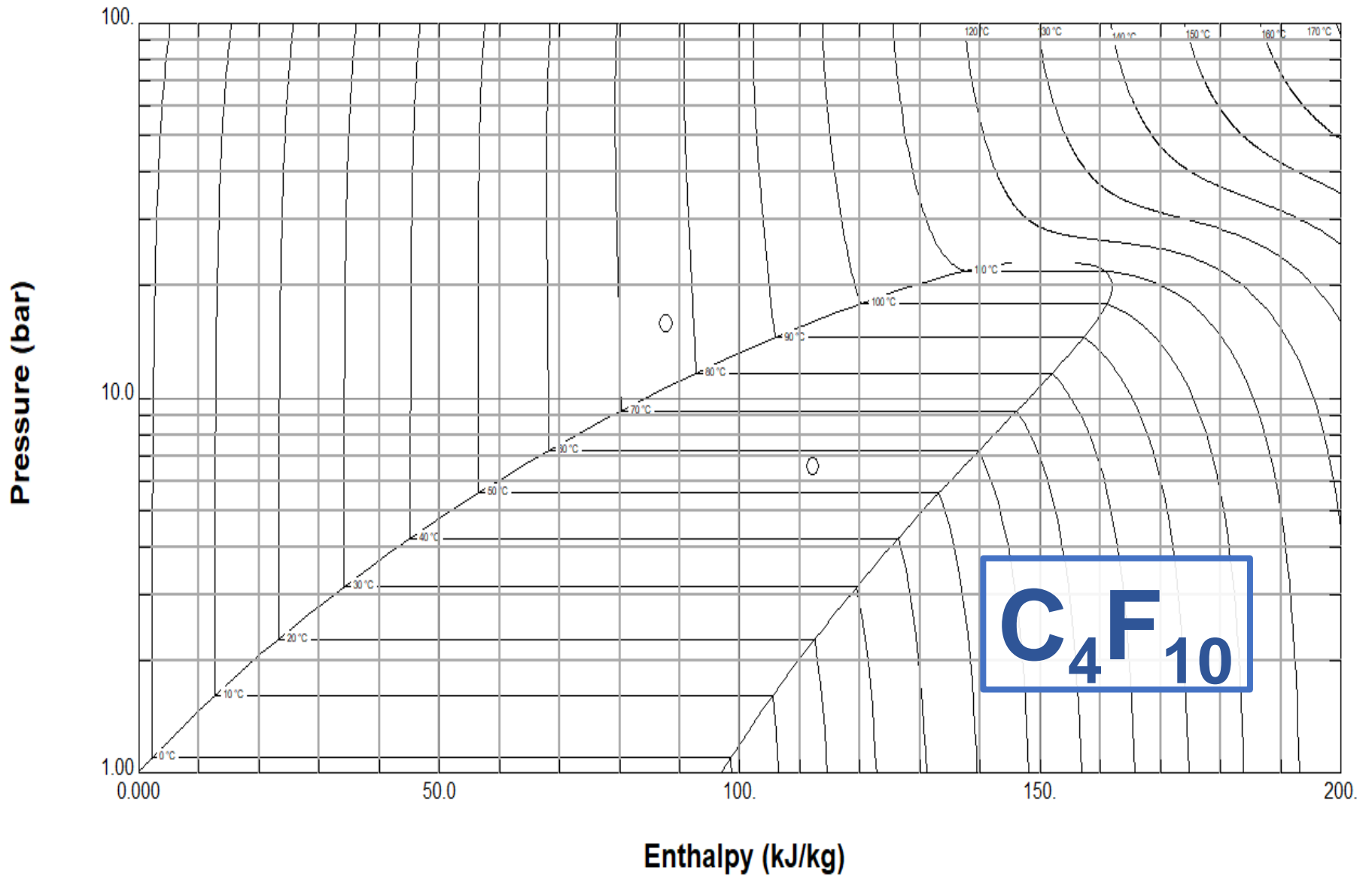
**Pressure-enthalpy plots for various  
Saturated fluorocarbons and blends  
(Circulation thermodynamics)**

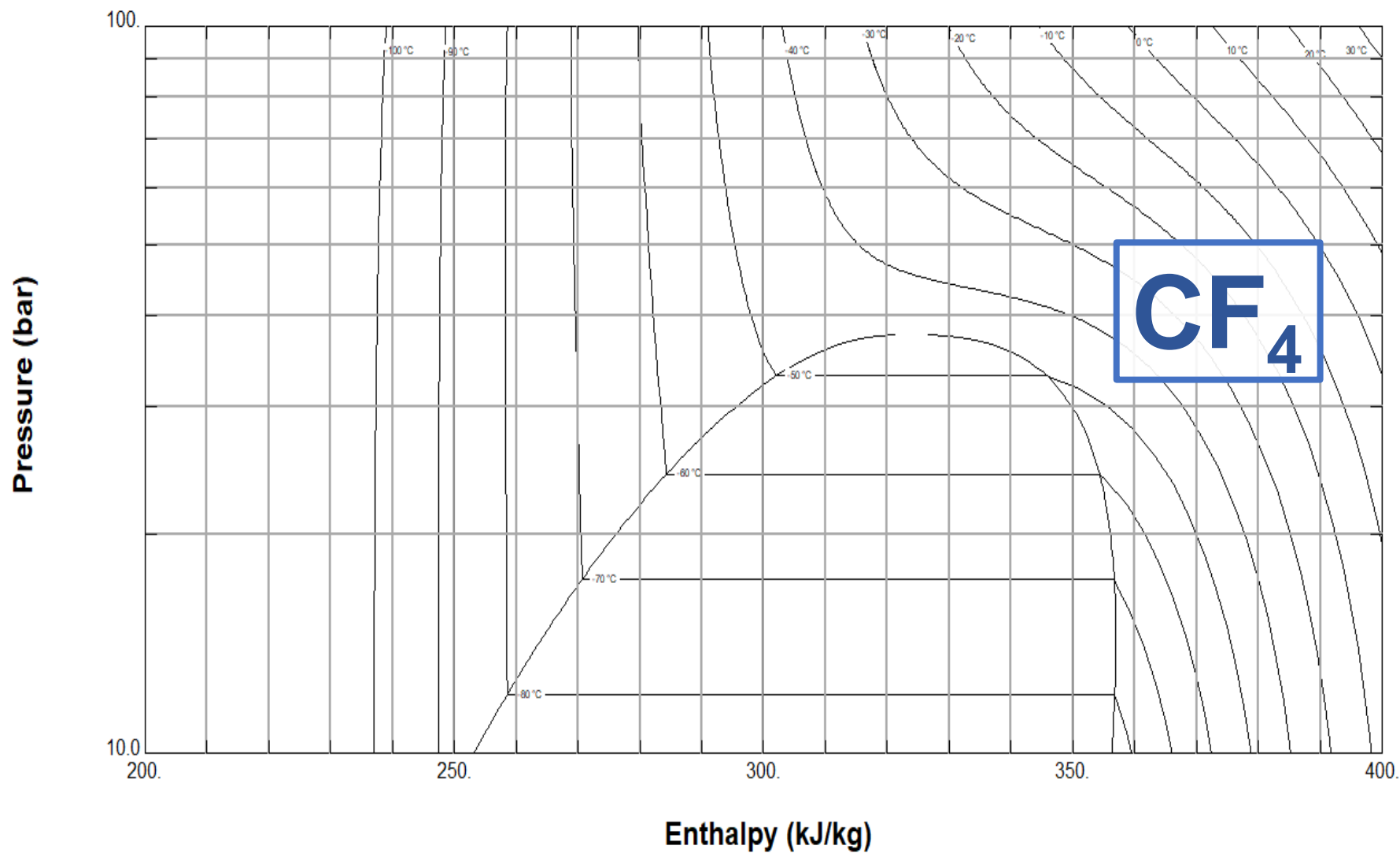
# LHCb: a two RICH (2 radiator) detector

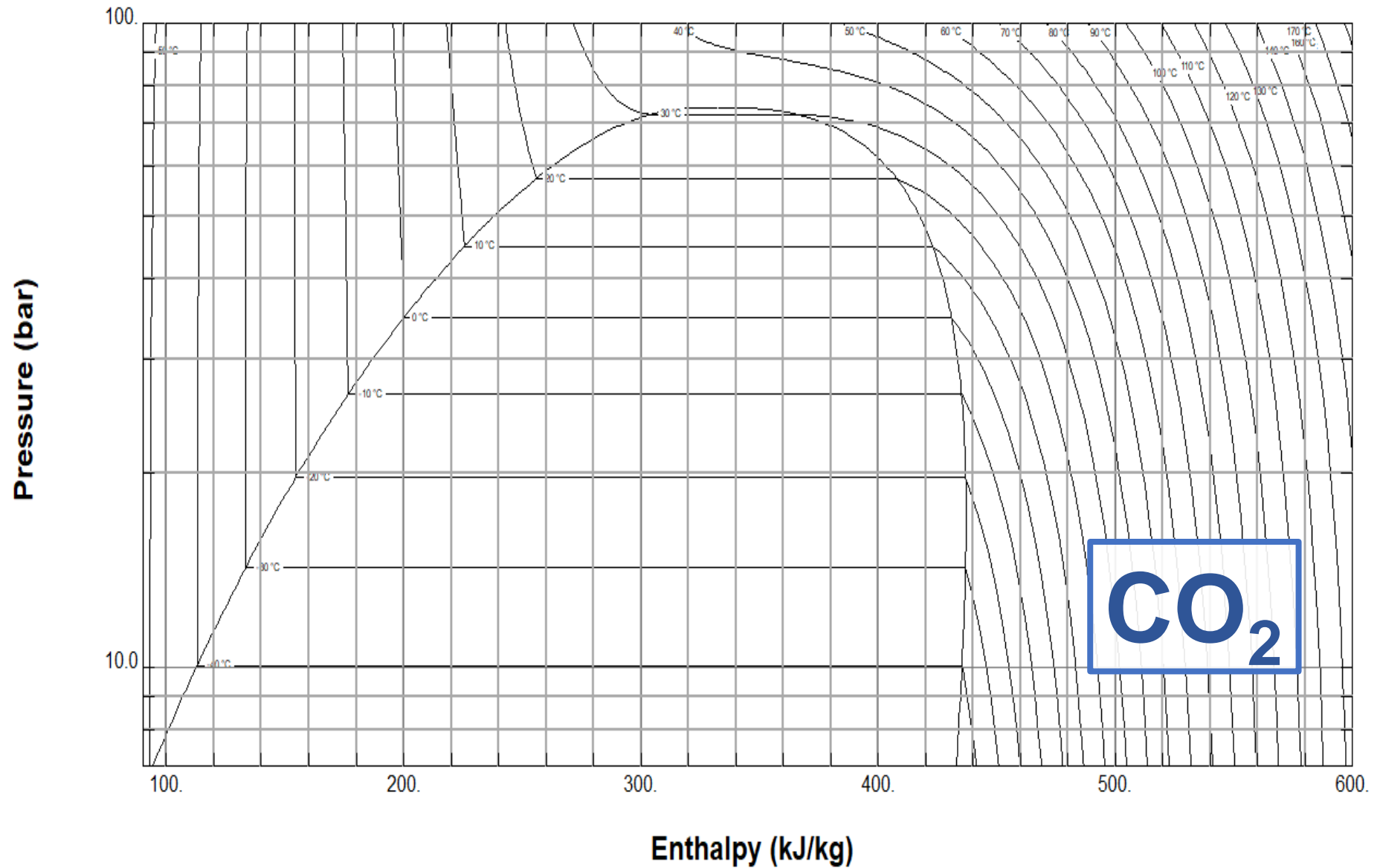
RICH 1:  $C_4F_{10}$  radiator: lower momentum PID  
 RICH 2:  $CF_4 (+CO_2)$  radiator: higher momentum PID

## COMBINED RICH PERFORMANCE & PARTICLE SPECIES IDENTIFICATION RANGE

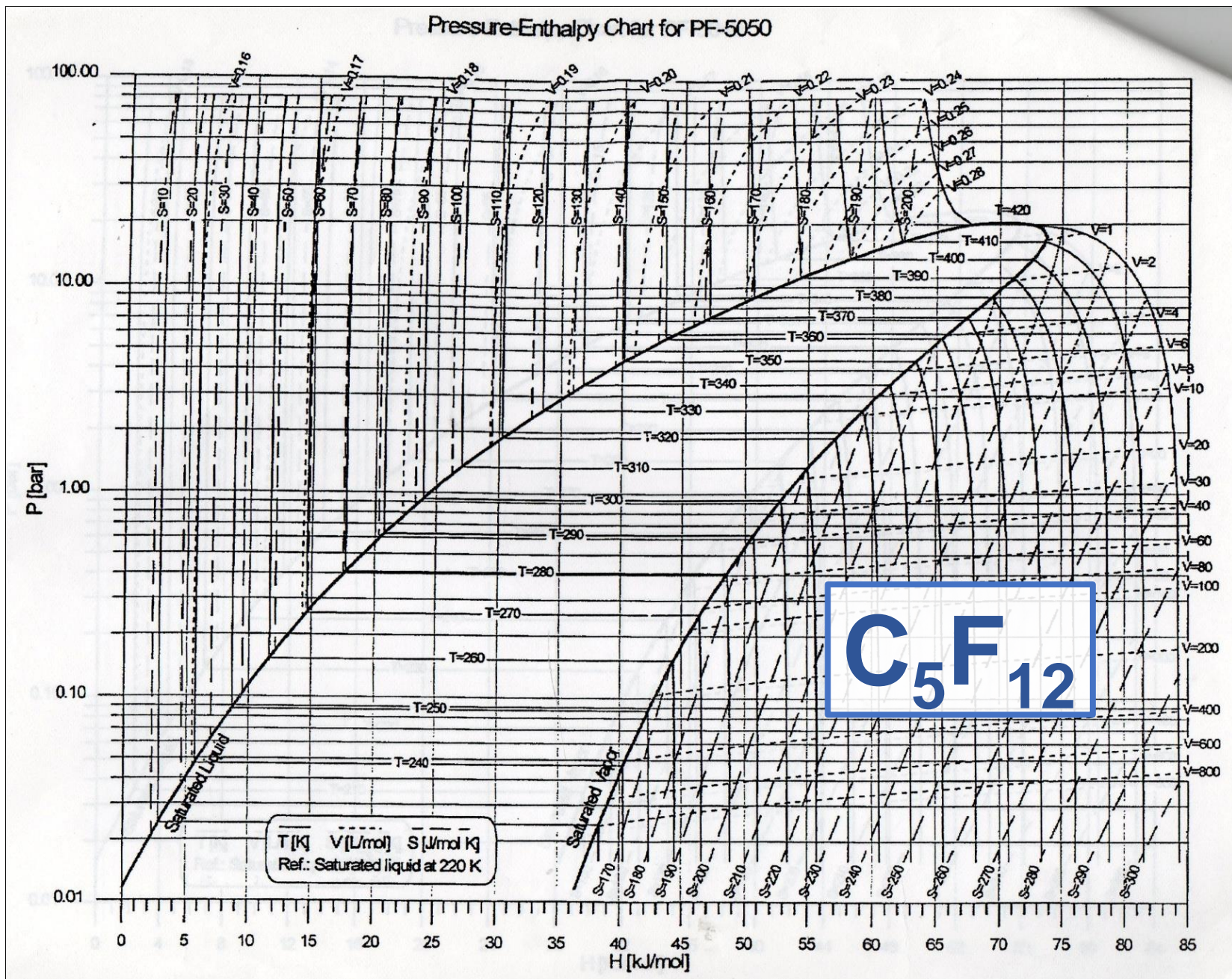






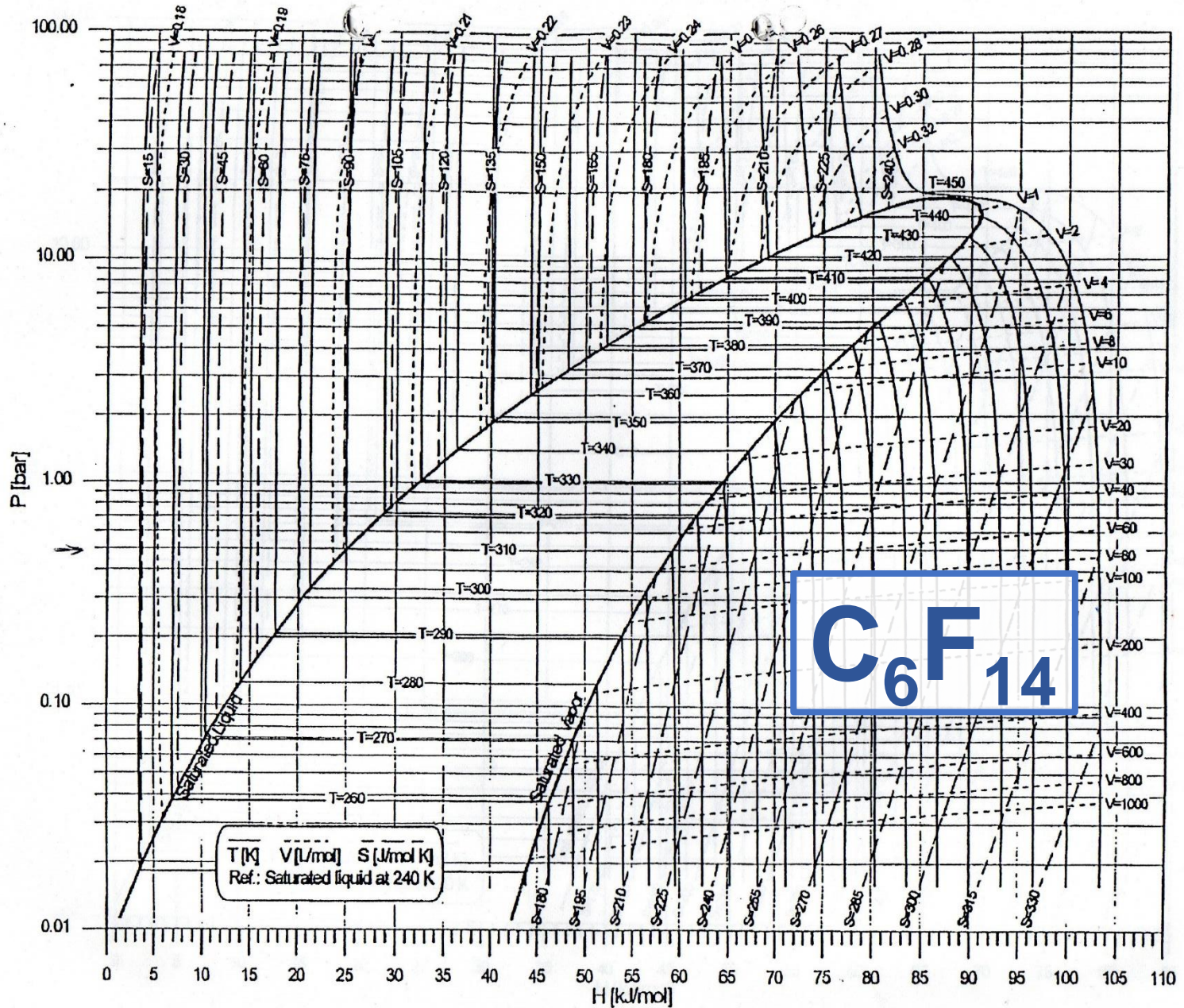




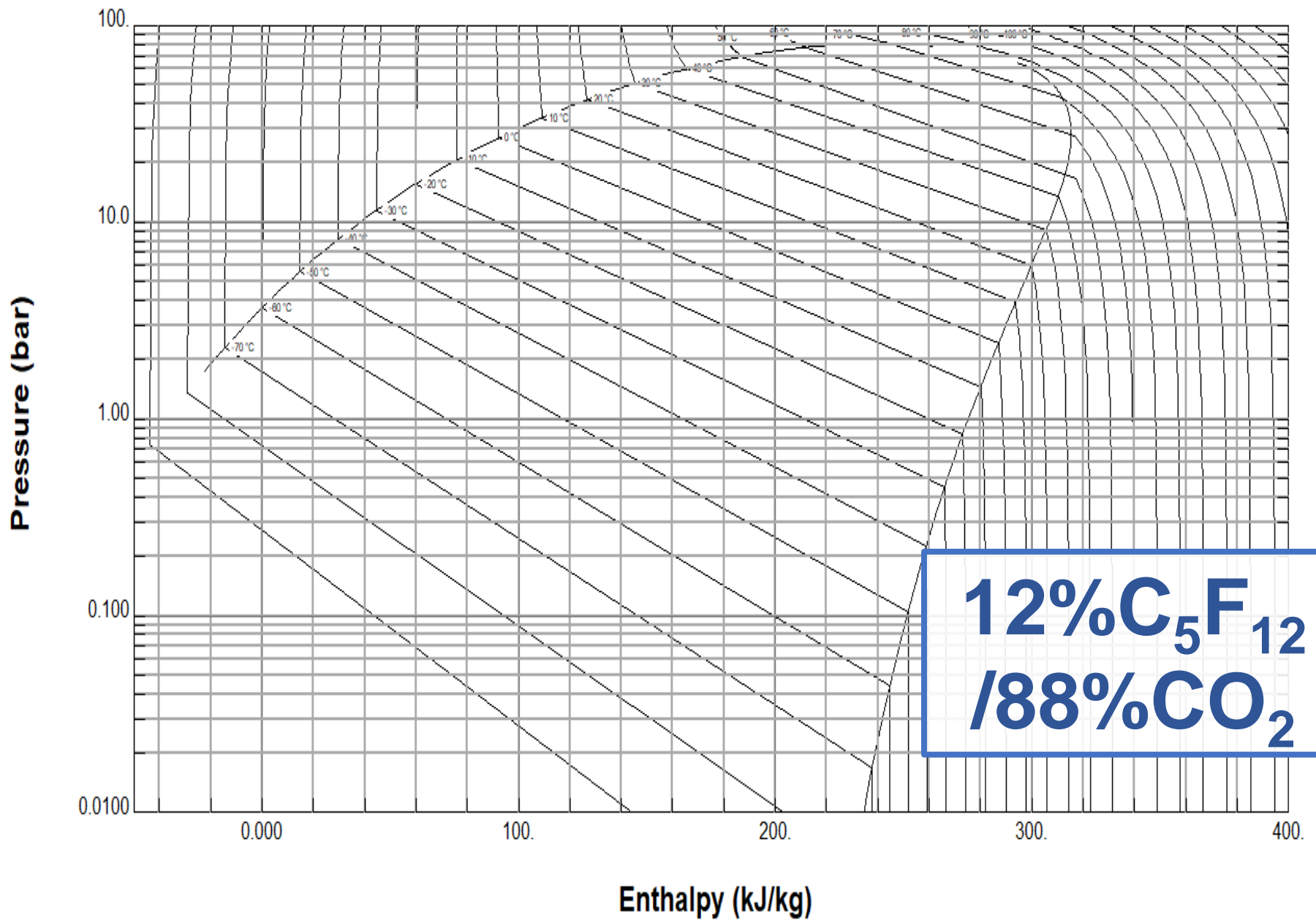


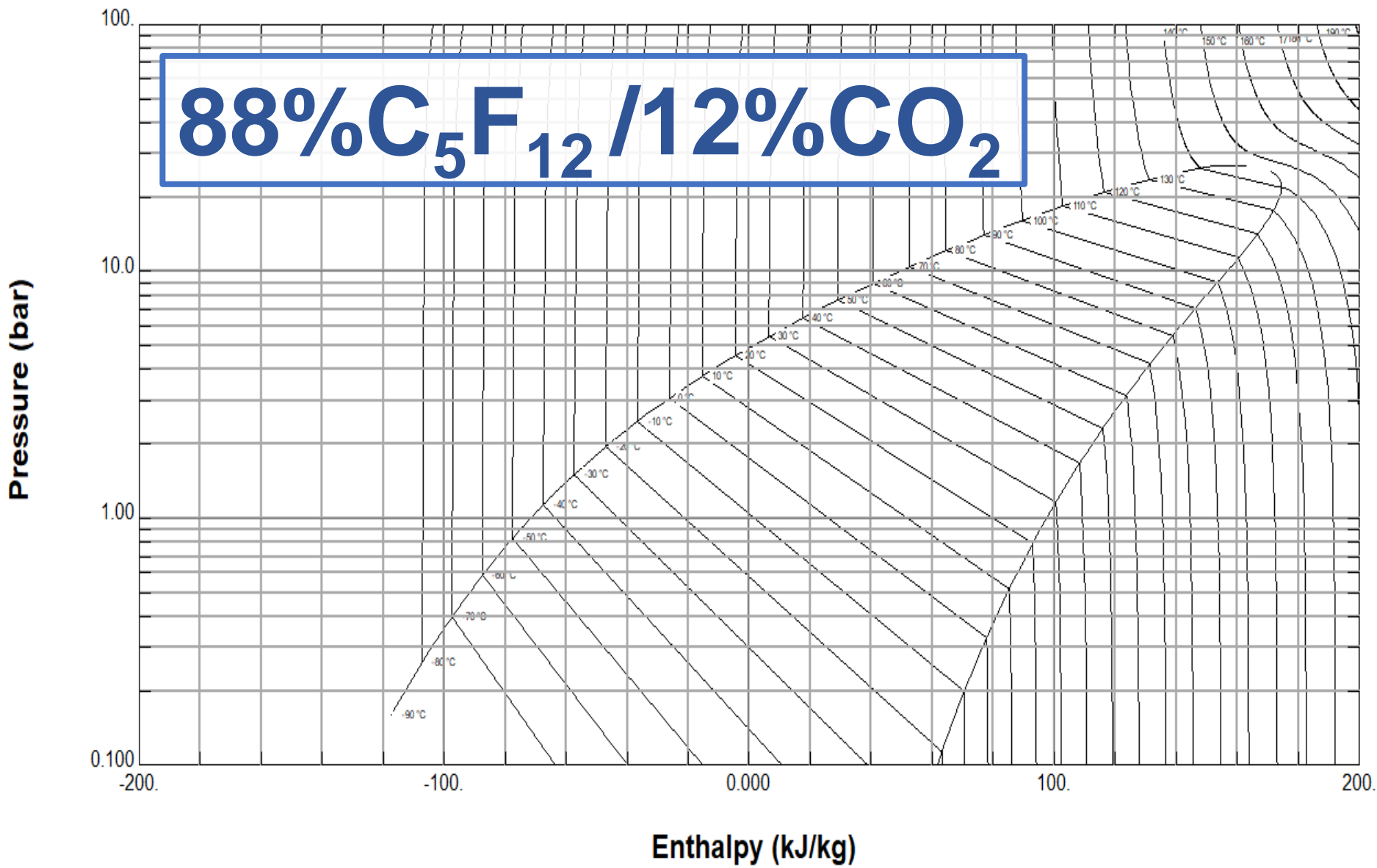


Pressure-Enthalpy Chart for PF-5060

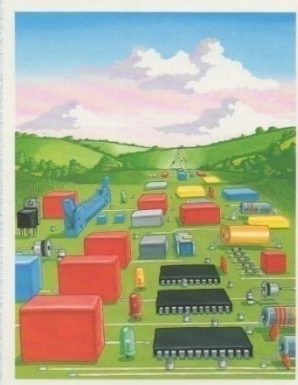








# Historical: fluorocarbons: military (mainly radar) and industrial uses (1)



## FLUTEC®



### Cooling

In situations where indirect cooling is insufficient to maintain constant temperatures within electronic equipment, direct contact with a liquid is an effective means of improvement. Heat removal can be considerably increased depending on the mode, e.g. pool-boiling is typically ten times as effective as convection. Consequently the direct cooling technique allows significant reduction in size and weight.

The technique is only possible with compatible fluids. The inert, non-flammable and excellent dielectric properties of FLUTEC compounds make them ideal candidates. FLUTEC PP3 has been particularly effective and has been very successfully used for



A Royal Navy Sea King helicopter fitted with the airborne early warning version of the Searchwater radar (Photograph by courtesy of Thorn EMI Electronics Limited).

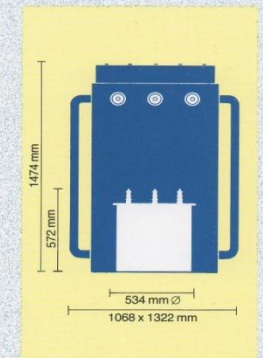
PP3	PP6	PP7	PP10	PP11	PP24	PP25
102	142	155	194	215	244	260
-70	a	-70	-40	-20	0	-10
400	462	512	574	624	686	774
1.828	1.917	1.972	1.984	2.03	2.052	2.049
1.06	2.66	3.25	4.84	14.0	15.3	56.1
1.919	5.10	6.41	9.58	28.4	31.5	114.5
16.6	17.6	18.5	19.7	19	22.2	
48	8.8	2.9	<1	<1	<1	<1
82.9	78.7	75.5	71*	68*	65.8*	67.9*
0.963	1.05	1.09	0.92*	1.07*	0.93*	0.957*
241.5	292.0	313.4	357.2*	377*	388.7*	400.4*
514.7	565.2	586.6	630.2*	650*	661.9*	673.6*
18.81	17.53	16.60	16.2*	14.6*	15.1*	11.34*
1.520	1.521	1.50	1.59*	1.58*	1.606*	1.574*
60.4	57.0	57.5	56*	52.6	64.6*	63.8*
0.00123	0.00104	0.00097	0.00078	0.00075	0.00078	0.00084
0.00178	0.00170	0.00167				
1.2895	1.3130	1.3195	1.3289	1.3348	1.3462	1.3376
405	417	422	429*			
(0.56)	(0.72)	0.796				
609	711		875*			

\* Estimated value.  
Temperature dependent properties are quoted at 25°C unless otherwise stated.  
a. Pour point - 8°C for typical cis/trans mixture.

many years by the British MoD in airborne radar. FLUTEC PP1C promises to be a useful material as a direct replacement for chlorofluorocarbon 113 in cooling applications.

Some of the applications for FLUTEC liquids include:-

- Radar transmitters
- Super computers
- Power supplies
- High voltage transformers
- Lasers



Reduction in transformer size achievable by replacing transformer oil with a Flutec liquid dielectric.



# Historical: fluorocarbons - military and industrial (heat transfer) uses (2)

SYSTEMS PACKAGING

## Cooling a Superfast Computer

Heat is removed from the CRAY-2 supercomputer by a cooling fluid that flows over each component.

By Richard D. Danielson, 3M Commercial Chemicals Div., St. Paul, Minn., Nick Krajewski and Jerry Brost, Cray Research, Chippewa Falls, Wisc.

A new generation supercomputer, the CRAY-2, uses a novel approach to cooling which will very likely influence computer construction in the future. Made by Cray Research Inc., the supercomputer combines diminutive physical size with very high speed and memory capacity.

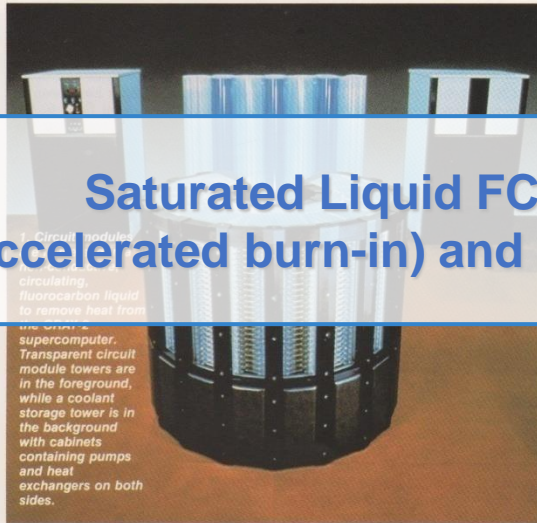
The new supercomputer is cooled by immersing the entire computer—cables, memory boards, logic circuits and main processors—in an inert, high-dielectric liquid bath. CRAY-2 works sit in a sealed 155-gal tank of 3M's Fluorinert perfluorocarbon, electronic liquid FC-77.

### Supercomputer packaging

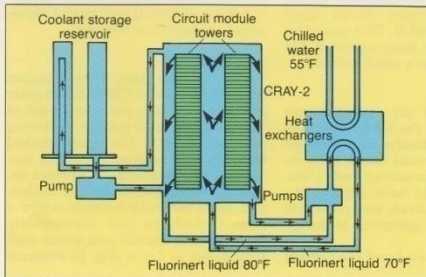
The CRAY-2 design makes use of significant technological innovations, with capabilities which are an order of magnitude greater than those of its predecessor. These include a clock cycle of 4.1 ns, four background processors for independent or combined tasking, high-speed local random-access memory of 256 million words, and an effective throughput six to 12 times that of the physically larger CRAY-1.

In dramatic counterpoint to its expanded speed and capacity, the CRAY-2 is only about half the size of Cray's earlier system, standing approximately 45-in. high with a diameter of less than 5 ft.

The CRAY-2's relatively small size is a necessity for its blazing speed. Signal propagation times from point-to-point within the system must be extremely short, or the exotic processor and memory circuits cannot do their job. But physical compactness creates enormous heat buildup problems. At very high computer speeds,



Circuit module towers are in the foreground, while a coolant storage tower is in the background with cabinets containing pumps and heat exchangers on both sides.



2. Cooling fluid is pumped through the circuit module towers and heat exchangers.

PRODUCTION TECHNIQUES

## Liquid Burn-In Testing Cuts TWT Supply Failures

Teledyne MEC in Palo Alto, Calif. is saving production time using liquid burn-in testing to detect traveling wave tube power supply failures before encapsulation.

By N.A. Kramer, Teledyne MEC, Palo Alto, Calif.

A liquid burn-in testing system employed prior to encapsulating units dramatically reduced failure rates in high-voltage power supplies at Teledyne MEC in Palo Alto, Calif. In some units the failure rate has fallen from ninety to five percent. The system uses Teledyne Fluorinert electronic liquid FC-43. It combines very low solvent action, high strength and excellent electrical characteristics. It also is non-flammable, non-explosive, and essentially non-toxic.

The company relies on liquid burn-in for testing all new designs and for troubleshooting high-voltage power supply modules or packages which are experiencing an unacceptably high failure rate. The test enables location and correction of any problems that may be encountered before encapsulation, when they can be corrected at minimal cost.

### Quick and inexpensive

Liquid burn-in testing is a quick and easy way of providing the temporary equivalent of encapsulation through immersion in a special liquid. While immersed in this liquid, the units are tested electrically. If defective, they are easily repaired and retested. If the burn-in test is passed, the units are then encapsulated in their permanent silicone coatings, and tested one last time before shipment.

Until the advent of liquid burn-in testing at Teledyne, high-voltage power supply modules were open-air bench tested. With this method, voltages had to be held to a minimum if the unit was unencapsulated, to avoid arcing and possible destruction. As a result, the unit's reaction to maximum load was left undetermined. In the event of failure, the encapsulating material had to be removed manually to locate and



1. In preparation for a burn-in test, a Teledyne technician connects a power supply to the unit under test. The liquid is then pumped into the liquid bath cabinet for full voltage tests. After testing, the liquid is recovered for reuse.

correct the problem. In addition to extra expense, there was an ever-present danger of causing greater damage in picking silicone out of the extremely compact power supply package.

To attain the high-voltage burn-in capabilities the company wanted—that is, subjecting unencapsulated units to maximum operating voltages—Teledyne engineers experimented first with a plastic battery case filled with FC-43. Units were immersed in the electronic liquid to pre-

vent arcing, but it was soon discovered that the liquid was a good insulator and also helped cool the units under test through excellent heat transfer properties.

### Excessive evaporation rate

Although this arrangement, which one engineer described as "jerry-rigged," worked fairly well, it did not permit extended burn-in of 24 to 48 hours at normal operating temperatures of 71° C to 105° C. At these temperatures, the evaporation rate of FC-43 liquid

Saturated Liquid FC immersion for destroying (accelerated burn-in) and preserving (cooling) electronics



# Historical - fluorocarbons: military and industrial (heat transfer) uses (3)

Liquides

## Fluorinert™

Soudage en phase vapeur

Le liquide idéal pour le soudage en phase vapeur.

### I - Procédé

Un contrôle précis de la température

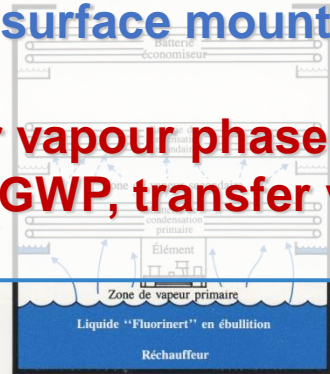
Le procédé de condensation de chaleur pour souder par reflux a été développé et amélioré un contrôle précis de la température, éliminant les nombreux désavantages présentes par les autres techniques de soudage par reflux.

### Description

En vue de réduire les pertes de liquide primaire par convection, diffusion ou par fuite, certains fabricants ont conçu dans leurs équipements une seconde zone de vapeur. Cette zone secondaire de vapeur est créée à partir d'un liquide de plus faible densité et de plus basse température d'ébullition.

Lorsque une pièce froide entre dans la zone de vapeur primaire, celle-ci enveloppe la pièce provoquant une condensation sur toutes les surfaces. Durant ce changement de phase (vapeur → liquide), la chaleur latente stockée dans la vapeur est transférée à la pièce, fournissant ainsi la chaleur nécessaire à la refusion. La soudure (pâte à souder, préformée) est appliquée

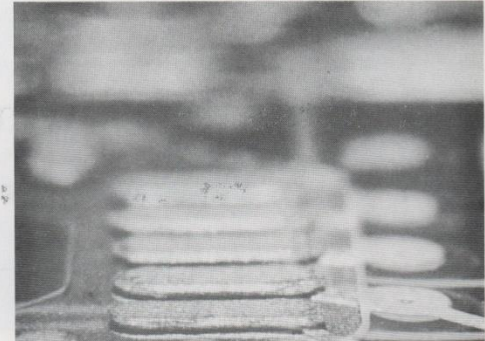
sur la pièce avant introduction dans la zone de vapeur. La soudure choisie doit avoir une température de fusion inférieure au point d'ébullition du liquide Fluorinert.



Surface Mount

## Fluxless SMD Soldering

one of the happier solder stories



## Vapour phase (non-contact) soldering of components on PCBs (particularly surface mount) in high T fluorocarbon atmosphere !!!

The demand for vapour phase soldering is hardly going to "evaporate". New, lower GWP, transfer vapours will be needed (e.g. NOVEC)

The need for leadless ceramic chip carriers has grown substantially in the past few years. These carriers significantly increase packaging density and reduce parasitic inductance and resistance to vibration than do conventional leaded carriers. Other approaches to mounting LCCs have been open to

question, but today vapor phase soldering is recognized as one of the most reliable solutions. VPS is an application of condensation heating to provide the heat needed to melt the solder. Even though the heat is developed by the condensing vapor, the board is not exposed to uniform heat, VPS provides a controlled, inert, and low temperature (215°C)

soldering environment. Even with the advantages inherent in the VPS process, flux residue can be difficult to clean from finished boards. It is not uncommonly reported that flux residue causes voids in solder joints because of its presence in the soldering process. Besides designing a method for removing flux, the best solution was to eliminate its use altogether.

### A Flux Shun

The engineering development group then set out to develop an LCC/MLB packaging technique with a fluxless assembly process. Besides designing a reliable process, an overall goal was to incorporate standard materials and techniques for cost containment and higher yields.

The cost of glass-epoxy printed wiring boards is considerably less than that of ceramic boards, so the group first tried standard glass-epoxy boards in

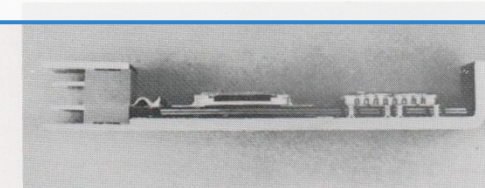
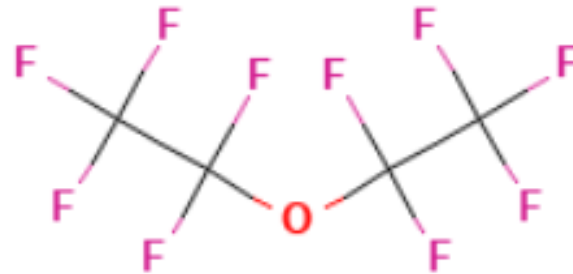


Figure 1 To lower the coefficient of thermal expansion of glass-epoxy multilayer boards, engineers at GE bonded alloy 42 — an iron/nickel mixture with 42% nickel — between board layers, as illustrated in this cross section of a LamCore MLB connector frame assembly.

Another linear all single-bonded geometry

$C_4F_{10}O$ ..? TO BEWARE???

**Bis(pentafluoroethyl)ether /  
Perfluoroethyl ether**



**GWP = ??**

Unfriendly (not nice to mice) & lachrygene

[https://pubchem.ncbi.nlm.nih.gov/compound/Bis\\_pentafluoroethyl\\_ether](https://pubchem.ncbi.nlm.nih.gov/compound/Bis_pentafluoroethyl_ether)

<https://www.govinfo.gov/content/pkg/CFR-2017-title40-vol23/xml/CFR-2017-title40-vol23-part98-subpartA-appA.xml>



# SynQuest Labs Inc.,

## 13201 Rachael Boulevard Rt 2054, Alachua, FL 32615, USA

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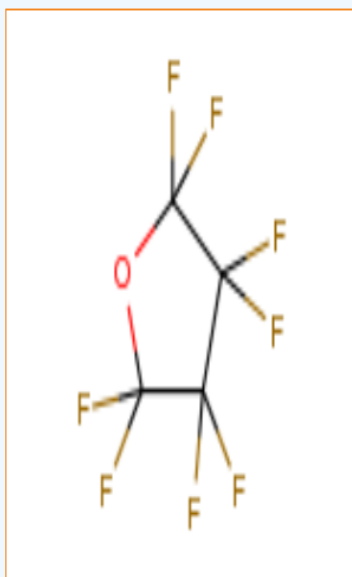
can manufacture different  $C_4F_8O$  configurations, including linear

<https://www.synquestlabs.com/Home/SearchProduct?pg=2&SearchName=1&SearchText=octa>



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## Octafluorotetrahydrofuran



**PN:** 2H07-2-08

**CAS:** 773-14-8

**Formula:**  $C_4F_8O$

### Available Units:

10 g/\$75

25 g/\$155

100 g/\$425

Bulk / [Contact for Price](#)

**The cyclic molecule seems to be cheaper for SynQuest to manufacture: whereas 3M make NOVEC 649, 5110 which are non-cyclic**