P. Gorbounov, M. Battistin, E. Thomas
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Comparison of liquid coolants suitable for single-phase detector cooling

Abstract

Three different classes of commercial heat transfer fluids (FK, PFCs and HFEs) are selected as candidates for the single-phase liquid cooling system of the SciFi Tracker photodetectors. None of them is perfect, though. PFCs are strong greenhouse gases: for example, C6F14, the popular PFCcoolant widely used at CERN because of its outstanding inertness and radiation resistance, has GWP of 9300. The heavier PFC fluid C7F16 with a wider liquid range has GWP of 7930. The 3M Novec fluids, designed as alternatives to PFCs and having sharply lower GWP, include a range of HFE liquids with GWP=60-300 and FK liquids, Novec 649 and 774, with GWP=1. These fluids are less inert and, arguably, less radiation resistant than PFCs. The 649, having the thermo-physical properties quite close to C6F14, had been tentatively selected as the baseline option for the SiPM cooling. HFE liquids Novec 7100 and 7200 can also be considered as alternatives. Environmental, safety and performance profiles of all above mentioned fluids are compared.

Nomenclature

HTF	heat transfer fluid	ROB	Read-out box
HTC	heat transfer coefficient	SciFi	Scinrillating Fiber (Tracker)
FOM	figure of merit	PFPA	Perfluoropropionic acid
HC	hydrocarbon(s)	SiPM	Silicon Photo-Multiplier
HFC	hydrofluorocarbon(s)		
PFC	perfluorocarbon(s)		
GWP	global warming potential		
C6F14	perfluorohexane C_6F_{14}		
FK	fluoroketone(s)		
C6K	C6-Fluoroketone, aka 3M Novec 649		
HFE	hydrofluoroether(s)		

1. Introduction

A single-phase liquid cooling for the SciFi tracker photodetectors [SciFi] was preferred to 2-phase cooling because of its lower cost, robustness, wider choice of coolants, more "off-the-shelf" cooling plant components (e.g., pumps). There were no compelling reasons to choose the more complex and demanding 2-phase technology, given the mostly passive thermal load of the SiPM read-out modules and the absence of severe material budget restrictions in this application. The freedom to choose the module connection topology[1] and reluctance to deal with high-pressure inside a fairly extensive system also favored the mono-phase choice. The environment-friendliness requirement alone was insufficient to opt, for example, for the "green" 2PACL CO2 cooling [Verlaat 2012].

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[1] The more economical serial connection was assumed at the TDR time. For the engineering design, the parallel connection of modules was preferred.

The initial idea was to use C6F14 as the coolant. This popular PFC fluid had been validated for the LHC [Battistin.1,3] and used in many detector cooling systems at CERN. Its unique combination of properties (inertness, non-flammability, ultra-high electrical resistivity, safety, radiation resistance, water-like pumpability at low temperatures outweighed its main drawbacks: poor heat transfer characteristics, the relatively low boiling point (57°C) and, most importantly, the high greenhouse potential (GWP = 9300 [Ivy 2012]), typical of all PFCs.

The environmental impact of C6F14 and other PFCs were tacitly disregarded compared to their obvious benefits for the design of the LHC detectors in early 2000. Now, on the eve of the LHC detector upgrades, the situation has changed. With globally growing environmental awareness, the environmental impact aspects cannot be ignored anymore (at least at the official level) and gradually become competitive with physics performance aspects. PFC emissions are now closely monitored at CERN [CERN GHG]. There are two strategies to reduce them: by anticipating and preventing the losses and by replacing PFCs with alternative fluids that are more "green".

Given the big size of the SciFi Tracker and the manifolding complexity, the inner cooling structures of ROBs and their interconnections[2], it will be difficult to make the SiPM cooling system totally "non-emissive" over the long term. Even in industrial applications [HFE.4], there are unavoidable operational losses related to the PFC's volatility and high thermal expansion (~ 1% per 10K). Thus, as long as we stay with liquid cooling, we have to count on a "green" solution as the baseline, while possibly keeping the cooling system (both detector and cooling plant sides) compatible with liquid PFCs, as a backup.

This memo summarizes our efforts to identify possible alternatives to C6F14 among modern commercially available fluids suitable for operation at -50°C and below. Unfortunately, no perfect reconciliation of environment- and application-friendliness seems possible for the SciFi application, so some sort of compromise is unavoidable. With C6F14 representing the extreme case of such a compromise, two other fluids have been shortlisted: the "TDR candidate" fluid 3M Novec 649, a FK with GWP of 1, and the HFE fluid 3M Novec 7100, with GWP of 320.

For completeness, we also consider close alternatives to each of the candidate, within the same class: the FK Novec 774 and the HFE Novec 7200. Even the PFC class contains liquids that are somewhat superior to C6F14, e.g. 3M FC-84 (C7F16) which has a bit lower GWP and a bit better thermal properties, while having a higher boiling point (80C) and, hence, lower evaporation losses.

2. Alternative coolants

2.1 What do we want?

The requirements for the fluid in indirect cooling systems are nicely summarized in Refs [Cengel 2007] and [Mohapatra 2006]: the ideal coolant is an inexpensive nontoxic liquid with excellent thermo-physical properties, a long service life and minimal regulatory constraints. It should be non-corrosive to the materials it comes in contact with. A high (or no) flash point and auto-ignition temperature are desired for safety reasons. Good thermo-physical properties (high thermal conductivity and specific heat, low viscosity) are required for the optimal heat transfer and low required pumping power.

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[2] Especially now that we are drifting to parallel, rather than serial, ROB connections and the 3D-printed segmented cooling bars with numerous connections.

Water, one of the best HTFs available, is an obvious example of a good approximation to the ideal. However, it is not suitable for cooling below water freezing temperature or applications requiring electrically non-conductive and clean coolant.

Electrical conductivity becomes important if the coolant may leak out of a cooling loop or be spilled during maintenance and come in contact with sensitive electronics. By the "cleanness", the ability to evaporate without leaving a residue that might attract dirt, deteriorate insulation or just irreversibly stain the setup is usually implied. DI water serves well for above-zero applications, though DI water based systems are usually quite expensive. DI water/glycol solutions are questionable because of their toxicity and "cleanness". The best attainable volume resistivities for DI water and DI/glycol are about 10^7 and 10^8 ohm-cm, respectively [DI]. We shall mark this level as the reference.

To that we have to add the application-specific requirements. The required operating temperature range should be well within the total coolant's liquid range[3]. For the SciFi cooling, the operating range is between -50°C (the lowest foreseeable working SiPM temperature) and +40°C (the SiPM annealing temperature).

The fluids for HEP detector cooling should be appropriate for working under radiation. This is not simply equivalent to requiring a superior radiation resistance for the coolant[4]. In practice, it rather means that the radiolysis products appearing in the coolant should not adversely impact the cooling system integrity and efficiency over the project's life time. When assessing this factor for indirect cooling, apart from the total dose and the radiation type, one has to take into account the pipe materials (metals, plastics, and elastomers), their geometry (e.g., wall thickness), the presence and efficiency of the filtering and purification elements in the cooling loop.

Traditionally, the radiation-related effects (especially for neutrons) were associated with the presence of hydrogen (H) in the coolant [Battistin] – because of the combined effect of the high neutron cross-section of H and potential hazards of acids produced by the radiolysis. For example, in fluorinated liquids the radiolysis chain involving hydrogen will result in formation of fluor-containing acids, e.g. HF, which, in combination with moisture, might cause corrosion of the metallic cooling system elements. Hydrogen can be present either in the coolant's molecule (like in HFEs), or in HC impurities, or in water dissolved in the coolant.

Obviously, the radiation-related requirements will be quite different for cooling of inner LHC detectors (with high radiation doses and thinnest possible heat exchanger walls) and for out-of-acceptance electronics (relatively thick-wall heat exchangers and low radiation doses, like in the SciFi tracker case). In [Gorbounov.1] it is shown that, even under exaggerated pessimistic assumptions, the radiolysis effect for a 3M Novec fluid in SiPM cooling system will be microscopic – simply because of the low expected ionization dose and neutron fluence. The resulting concentration of acids will be low and the dominant radiation damage in this case will be associated with the impurities, rather than with the coolant itself. Similar arguments are applicable to any other fluid with no or low H content. Thus, the "no hydrogen" requirement can

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[3] The range between the pour and boiling points at the operating pressure.

[4] According to my survey at CERN, people often refer to clichés, like "C6F14 is radiation-hard". The very notion of "radiation resistant" object has no universal definition and is interpreted differently when applied to biological objects, electronics (e.g. semiconductors) and construction materials. The common meaning is a property to preserve its principal functionality under exposure to a certain level of ionizing or neutron radiation. The difference between "radiation resistant" and "radiation hard" is also fuzzy. In any case, the criteria of "radiation resistiveness/hardness" are very much different for liquids and solids.

be tentatively lifted, as one of possible compromises. Our search for the SiPM coolant follows this hierarchy of criteria:

1. Commercial dielectric liquids
2. CERN regulations: non-flammable (no or high flash point[5]), non-toxic
3. Clean (no pollution of the workplace)
4. Operating temperature range: -50…40°C
5. Stable, non-corrosive (according to MSDN)

The shortlisted candidates are ranked according to their environmental, thermal transfer properties, pumpability, cost and safety, as well as material compatibility and reactivity.

2.2 What do we have?

A concise overview by S. Mohapatra [Mohapatra 2006] described the main classes of commercial liquids for electronics cooling. Current catalogues of leading coolant manufacturers, like 3M, DuPont, Solway Solexis, Dynalene, Exxon, indicate that the industry did not offer qualitatively new classes of fluids since the last major environmental policy shift which occurred after the Kyoto protocol entered into force in 2005. The industrial R&D efforts, quite expectedly, were aimed at gaining the market for the mainstream applications, like air conditioning, power electronics and data center cooling, semiconductor manufacturing, home heating etc., which mostly belong to the above 0°C or 2-phase cooling domains. A renaissance of interest to CO2 cooling is also observed, especially in the mobile air-conditioning sector [CO2-AC]. As to low-temperature single-phase applications, the only visible new "development" since mid-2000s was the addition of FK fluids, originally positioned as fire-fighting agents, to the HTF category, under new trade names (e.g. Novec 649, formerly known as Novec 1230).

Here are the main classes of stable electrically insulating[6] coolants[7] that are liquids at a room temperature, with remarks on their safety, environmental and operational profiles:

- **Aromatics (HC):** Synthetic hydrocarbons of aromatic chemistry. These compounds are usually highly flammable and cannot be classified as non-toxic. Often they have strong odours, which can be irritating to the personnel.   Temperature range: at or above room temperature, but some, like (diethylbenzene-based?) Paratherm CR, Dynalene MV, Dowtherm J, are good down to below –80°C, see Refs. [HC.1,2,3]

- **Silicate-ester (SE):** These synthetic liquids (i.e., Coolanol 20, 25R, Refs. [SE]) were widely used as a dielectric coolant in military radar and missile systems. SEs have caused significant and sometimes catastrophic problems due to their hygroscopic nature and subsequent formation of flammable alcohols and silica gel. They are being replaced by aliphatic chemistry (polyalphaolefins or PAO).

- **Aliphatics (PAO):** Aliphatic hydrocarbons of paraffinic and iso-paraffinic type (including mineral oils) are petroleum-based fluids. They are non-toxic, have a non-discernible odour, and do not form hazardous degradation by-products. PAOs directly replaced the silicate-ester fluids in a variety of military and avionic applications. Example: Dynalene HF-LO [PAO] (according to data sheet, is good down to -73C but

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[5] The temperature at which the vapors produced from a fluid will ignite (flash-off) with the presence of an ignition source (the fluid will not burn at this point).
[6] Below, the term "dielectric" will be used in the sense "electrically insulating", like in most of literature on liquid coolants.
[7] DI water and DI-glycol mixtures are excluded because of poor stability of their electrical insulating properties and limited usability below -25C.

combustible and toxic). Most PAO fluids have prohibitively high viscosity below 0°C [Tuma 2009].

- **Silicones:** A popular coolant chemistry is a liquid polymerized siloxane (e.g.,dimethyl (or ethyl, or phenyl) polysiloxane) commonly known as *silicone oils*. The molecular weight and the thermo-physical properties (freezing point and viscosity) of this synthetic polymer can be adjusted by varying the chain length and configuration. Silicone fluids are used, as lubricants and HTFs, at temperatures as low as -100°C and as high as 400°C. They are excellent dielectrics, nontoxic and stable within the design temperature range, have low odour. Dimethylsiloxanes feature relatively good radiation resistance (up to ~10 kGy) and phenylsiloxanes withstand up to 1 MGy []. Julabo recommends silicone oils as standard coolants [Sil oils.1] for their open-bath chillers. However, low-temperature silicone oils are expensive, flammable and, because of low surface tension and low vapour pressure, very polluting liquids. Examples: Dow Syltherm XLT, Julabo Thermal HY, Gelest Silicone Fluids, see Refs. [Sil oils].

- **Fluorinated liquids[8] (PFC, PFE, HFE, FK)** have certain unique properties: first of all, unlike all other dielectric fluids, some of them are non-combustible, non-toxic and very inert. Secondly, some of these fluids have low freezing points and low viscosities at very low temperatures. In addition, unlike silicone oils, they are "clean" (in the sense discussed above). On the negative side, all these liquids are very expensive and have quite poor thermal properties as single-phase coolants. In addition, PFCs and PFEs are greenhouse gases. Due to the extremely low surface tension and incompatibility with fluoroplastics, fluorinated liquids will easily develop leaks in the systems that are not specifically designed for their use. Their volatility may result in high operation costs.

The only truly non-flammable dielectric fluids are found among fluorinated compounds. Silicones could be considered, as well, because their flammability is quite low and the low flash point (e.g., 42°C for Syltherm XLT) is offset by extremely poor volatility. However, silicon oils are famous for their property to badly pollute the workplace in case of a spill. This is the main reason that prohibits their use in large-scale systems. The aggregate heat transfer performance of silicone oils at low temperatures is not better that that of PFCs (see Section 3.1), while the pumpability is by order of magnitude worse.

Thus, we are left with a handful of fluorinated heat transfer liquids suitable for operation at -50°C (and below). At first look, they are quite similar, all having zero ODP and being much heavier than water, stable, inert, very fluid and volatile. They all have rather poor heat transfer properties and do not differ much from each other in that respect (see Section 3.1). The first and main difference between them is in their GWP:

- PFC: C_6F_{14} and heavier linear or branched perfluoroalcanes (from 3M Company, F2 Chemicals, several other minor suppliers) are potent greenhouse gases with GWP of 8000…9300 (very bad);

- HFE: segregated HFE fluids produced exclusively by 3M Company as Novec 7000-series are environmentally safe with GWP from ~50 to ~330 (good);

- FK: C6- (3M Novec 649, Novec 1230) and C7- (3M Novec 774) fluoroketones both have GWP ≈ 1 (excellent).

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[8] Commercial HFC (e.g. HFC-134a) and HFO (e.g. HFO-1234yf) fluids massively used in 2-phase air conditioning systems are gases at normal conditions.

The huge spread in GWP does not come for free: unlike really inert PFCs, both HFE and FK fluids have minor issues at the chemistry level. In addition, they have lower electrical resistivity compared to PFCs and, arguably, lower radiation resistance. However, these drawbacks are not dramatic and leave room for compromises, as will be discussed in the following Sections.

All these fluids are available from the same supplier, 3M Company [3M HTF], and the rest of this memo is based on the 3M documentation (Product Information brochures, MSDSs, articles and reviews) available from open internet sources.

2.3 PFC fluids: C6F14 and C7F16

C6F14 and other PFC fluids are supplied by 3M under the brand name Fluoroinert Electronic Fluids. C6F14 comes as FC-72[9] [PFC.1]. Other Fluoroinerts suitable for SiPM cooling are FC-84 (C7F16 and isomers, [PFC.2]) and FC-770 [PFC.3]. We shall consider only FC-84 as an alternative to C6F14 in this class, as no sufficient amount of technical data is available for FC-770. PFC liquids, as a class, have extremely high electrical resistivity, $\sim 10^{15}$ Ohm·cm – better than air and comparable with FR4 ($< 3.3 \cdot 10^{14}$ and $\sim 10^{14} \ldots 10^{15}$ Ohm·cm, respectively).

2.4 Hydrofluoroether fluids

Segregated hydrofluoroethers (HFEs), supplied by the 3M Company [3M HTF] as Novec 7000-series fluids, have an excellent blend of thermal transport, safety, and environmental properties that make them good candidates for a secondary heat transfer system. They share many of the valuable performance properties of PFCs and are positioned by 3M as sustainable alternatives to PFCs, with much lower GWPs. Concise reviews of these fluids can be found in Refs [HFE.4,5]. 3M provides practical guidelines for the HFE-based cooling systems design [HFE.5] and explicit recommendations on materials to be used in such systems [HFE.6].

For practical purposes relevant to heat transfer, Novec HFE fluids differ from Fluorinert fluids in their chemical structure, hydrocarbon solubility and electrical properties [HFE.6]. Unlike PFC, the HFE molecules contain one oxygen and a few hydrogen atoms. In segregated HFEs, patented by the 3M, the perfluorinated portion of the molecule is "segregated" from a fully hydrogenated portion by oxigen atom (an "ether" linkage). The presence of hydrogen in the molecule makes this compound susceptible to OH radicals that break it in the troposphere, which predetermines their short atmospheric lifetime and the lower GWP. It also makes the molecule a good solvent for hydrogenated materials, in particular – for HC-based pasticizers in elastomers. Like PFCs, the HFE fluids can also dissolve other fluorochemicals, while featuring a good compatibility with metals, hard plastics and unplasticized elastomers.

Novec HFEs are very stable, do not hydrolize, have no flash point and are non-toxic (see Section 3.4).

Novec HFEs are good dielectrics but their resistivity (10^8-10^9 Ohm·cm) and dielectric constant (~ 6-7 at 1 kHz)[10] may fall short in some high-voltage or high-frequency applications with direct cooling, where PFCs would be eligible.

As heat-transfer media, the HFE fluids are becoming increasingly popular in direct cooling (also referred to as pool-boiling and full-immersion [PoolBoiling.xx]) applications when the above limitations are not critical, in particular, in a very rapidly growing bitcoin mining [PoolBoiling.2]

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[9] It is also available as one of 3M Performance Fluids, the PF-5060; CERN uses PF-5060, which is, essentially, identical to FC-72.
[10] Compared to $\sim 10^{15}$ Ohm·cm and ~ 1.9, respectively, for PFCs.

and electric car (battery cooling [Kaiser.1]) industries. This fact can be regarded as a practical proof of the excellent compatibility of the HFEs with various materials, including elastomers and plastics, under normal conditions and at elevated temperatures.

No open information about radiation resistance of HFE is available.

We shall consider two Novec HFE liquids suitable for the operating temperature range between –100C and 50C: Novec 7100 [3M 7100] and Novec 7200 [3M 7200], having GWPs of ~300 and ~60 and boiling points of 61°C and 76°C, respectively.

2.5 Fluoroketone fluids

C6-fluoroketone (C6K) fluid 3M Novec 649, featuring a record low GWP=1 and the thermo-physical properties quite similar to those of C6F14, had been tentatively selected as the baseline solution for the SiPM cooling in SciFi. One known issue with this fluid is its weak reactivity with liquid water (i.e., a separate water phase): it hydrolyzes producing an organic acid, PFPA. This is not an immediate issue for the intended application because of the sub-zero working temperature, the presence of moisture and acids filters and the use of corrosion-resistant materials (e.g. SS or titanium alloy) for tubing and cooling structures in the future system. The system design will also aim at avoiding water condensation or frost deposition on the inner and outer surfaces of the cooling system, thereby reducing the risks of direct contact with moisture in case of minor leaks. These risks are further reduced by a very high volatility of the C6K. An in-depth validation of C6K at CERN is foreseen [WP2015].

As a fire-suppressing agent 3M Novec 1230, C6K was present on the market long before joining the HFT category. The vast available literature about C6K is reviewed in Ref. [Gorbounov.2]. As a HTF, C6K is primarily intended for immersion cooling (pool boiling) applications[11], because of its relatively low normal boiling point (49°C). In about 2012, 3M introduced another FK fluid, Novec 774 [3M C7K], which is a mix of isomers with 7 carbons (C7K). It features a higher boilng point, 74°C[12], and, otherwise, is quite similar to C6K (in particular, has GWP≈1). FKs are very good dielectrics (~10^{12} Ohm·cm).

Unfortunately, there is no published data about their radiation resistance of FKs. The low GWP is due to a photolysis at a near UV (with the absorption peak at 307 nm). The relatively weak C-C bonds adjacent to the carbonyl group in the C6K molecule might cause a reduced resistance to ionizing radiation [Taborelli 2014], which, if confirmed, will probably limit the use of FKs to low-dose detector cooling applications, unless very efficient online rectification (acid removal) methods for C6K will be designed as part of the validation study.

3. Comparison of selected coolants

3.1 Heat transfer and hydraulic properties

A traditional probe for evaluating coolant performance is a simple model of a straight round cooling pipe coupled to a process, with a developed laminar or turbulent inner flow. Within this model, the "target" system parameters are computed as functions of the "input" system parameters, like the fluid velocity (v), the pipe hydraulic diameter (D), the pipe length (L), the process heat load Q etc. Frequently used "target" parameters are

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[11] This indirectly indicates a broad material compatibility of Novec 649, especially given that this cooling method is aimed at large data centers in hot climate conditions.

[12] The boiling point values are reflected in the trade names of the 3M FK fluids. The prefix "6" or "7" stands for the number of carbons in the molecule.

- h, the heat transfer coefficient (HTC),
- Δp, the pressure drop,
- P, the pumping power,
- ΔT and Δt , the temperature drops along and across the pipe, respectively.
- Aggregate estimators, like Yeh-Chu number $c_p h/P$, coefficient of performance Q/P etc

The choice of "targets" and "inputs" is more or less arbitrary, because all these parameters are correlated. The fluids are compared to each other by computing dimensionless *ratios* of the corresponding "target" parameters. If one fluid is taken as the reference, such ratios can be regarded as figures of merit (FOM) for other fluids.

The following FOMs, having clear interpretations for our application, are used in the present work[13]:

- r_{hv}, the ratio of HTCs, for the comparison with the same flow velocity, $v_1/v_2 =1$. This is, perhaps, the most frequently used FOM. The fluid with $r_{hv} > 1$, for the same flow rate, will have a smaller Δt compared to the reference and require lower input temperature for the same process temperature. r_{hv} *depends on all four properties ρ, k, c_p and μ .*

- $r_{\Delta pv}$, the ratio of pressure drops Δp, for the same flow velocity, with $v_1/v_2 =1$. It is another simple FOM, often used together with r_{hv}, (see, for example, Ref. [FOM.xx]). The fluid with $r_{\Delta pv} < 1$, for the same flow rate, will have a smaller pressure drop Δp. $r_{\Delta pv}$ *depends only on ρ and μ .*

- r_{hP}, the ratio of HTCs, for the constant pumping power comparison, with v_1/v_2 determined from the $P_1 = P_2$ constraint. The fluid with $r_{hP} > 1$, for the same pumping power, will have a smaller Δt compared to the reference and require lower input temperature for the same process temperature. r_{hP} *depends on ρ, k, c_p and μ .*

- $r_{h\Delta T}$ and $r_{P\Delta T}$ – ratios of HTCs and pumping powers, for a comparison with the same temperature drop along the pipe. They are relevant for our application, because apart from requiring a certain average process temperature, we impose a limit on the temperature non-uniformity along our process (the detector array) which is correlated with the longitudinal fluid temperature drop. As an example, we can require ΔT=4°C.[14] The $r_{h\Delta T} > 1$ and/or $r_{P\Delta T} < 1$ indicate that a fluid will have a smaller lateral Δt and/or require a lower pumping power, compared to the reference fluid. $r_{h\Delta T}$ *does not depend on ρ, while $r_{P\Delta T}$ does not depend on k.*

- $r_{x\Delta T}$, the ratio of Yeh-Chu numbers ($c_p h/P$). This estimator was suggested to express the desire to maximize the heat storage (c_p) and heat removal (h) capabilities, while at the same time minimizing the required pumping power (P). A trivial constraint $v_1 = v_2$ usually used in the literature is replaced here with a more appropriate $\Delta T_1 = \Delta T_2$ constraint, like in $r_{h\Delta T}$ and $r_{P\Delta T}$.

C6F14 is used as the reference liquid in all FOMs. In addition to the fluorinated liquids described in Sections 2.3, 2.4 and 2.5, a representative silicone oil (Syltherm XLT) is included in the comparison.

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[13] All technicalities are described in Appendix A.

[14] This will approximately correspond to the maximal tolerable temperature drop of 1°C per a group of 4 SiPMs. Note, that FOMs with fixed ΔT might be not meaningful for other applications, like brine systems.
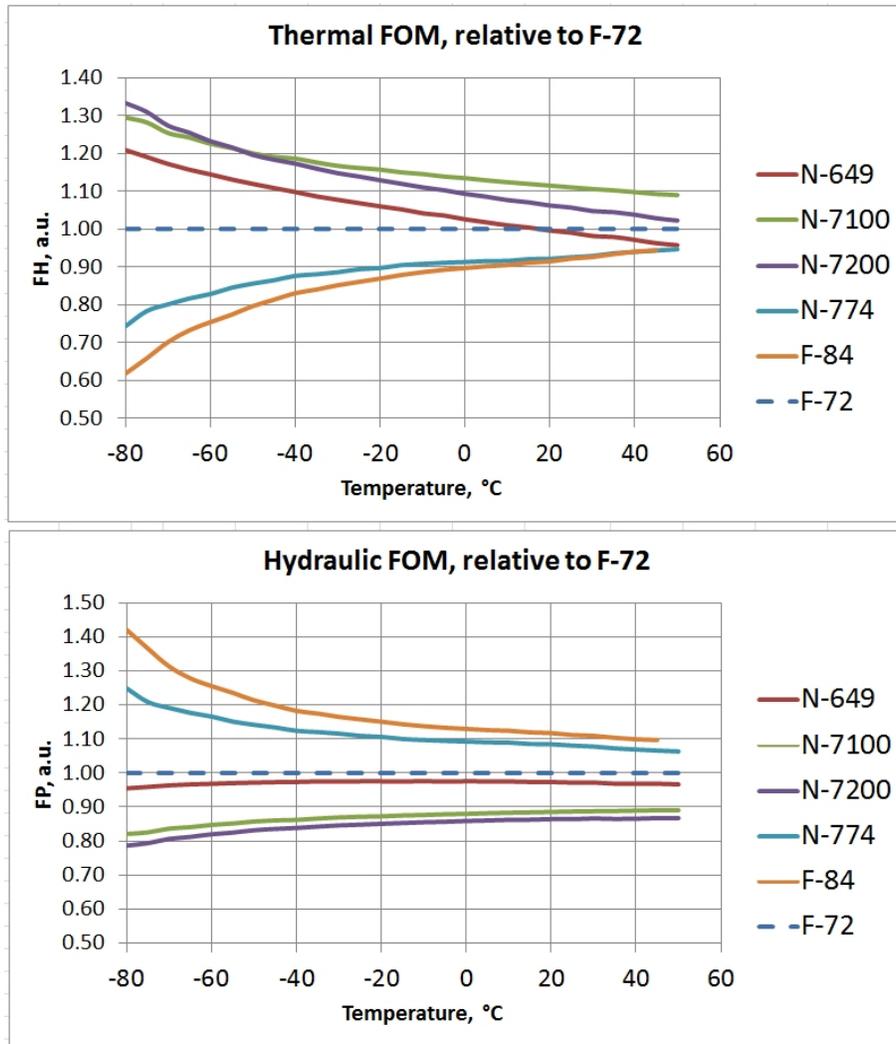
Figure 1: Comparison of r_{hv} (top) and $r_{\Delta pv}$ (bottom) for different coolants, as functions of fluid temperature.

3.2 Chemical reactivity

To be written

3.3 Material compatibility

To be written

3.4 Safety

Table 1 shows a compilation of safety information for selected liquids, mostly taken from the corresponding MSDS (Material Safety Data Sheets). The highlighted positions correspond to the "best in category".

Table 1: Comparison of MSDS (Material Safety Data Sheets) data for selected coolants

	Fluoroinert FC-72	Fluoroinert FC-84	Novec 7100	Novec 7200	Novec 649	Novec 774
Chemistry	PFC	PFC	HFE	HFE	FK	FK
Principal compound(s)[15]	C6 (C6F14)	C7 (C7F16)	CAS 163702-07-6, CAS 163702-08-7 (C4F9(O)CH3)	CAS 163702-05-4, ??? (C4F9(O)C2H5)	CAS 756-13-5 99.9±0.1% (C6F12O)	CAS 813-44-5, CAS 813-45-6 (C7F14O)
GWP	9300 [Ivy 2012]	7930 [Ivy 2012]	320	55	1	1
Boiling point, °C	56 (50…60)	80 (75-90)	61	76	49	74
Flash point	NA	NA	NA	NA	NA	NA
Auotoignition T, °C	NA	NA	405	375	NA	NA
Lower Explosive limit, %	NA	NA	NA	2.4	NA	NA
Vapor density wrt Air, at normal conditions	11.7	13.4	8.6	9.1	11.6	no data
Reactivity[16]	some	some	some	norm	some	some
Incompatibility with materials and conditions to avoid	active metals, alkali, alkaline earth metals	same as for FC-72	strong acids, strong bases, strong oxidizing agents	same as for Novec-7100	strong bases, alkohols, amines, water, direct sunlight/UV	strong bases, amines, alkali, alkaline earth metals
Hazard Classification[17]:						
NFPA (He/Fl/Re/Spec)	3/0/0/none	3/0/0/none	3/0/0/none	3/1/0/none	3/0/0/none	3/1/1/none
HMIS(He/Fl/Re)	0/0/0	0/0/0	1/0/0	1/1/0	0/0/1	1/1/1
US Fed. Regulations[18] *Fire/Pres/React/Imm/Delay*	N / N / N / Y / N	N / N / N / Y / N	N / N / N / Y / N	N / N / N / Y / N	N / N / N / N / N	N / N / N / Y / N

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[15] C6 and C7 means: a mix of PFCs, predominantly with 6 and 7 carbon atoms, respectively

[16] "Some" reactivity means: This material may be reactive with certain agents under certain conditions; "Norm" means: This material is considered to be non reactive under normal use conditions

[17] NFPA: US National Fire Protection Association rating (Health / Flammability / Reactivity / Special hazards), from 0 (none) to 4 (danger) [NFPA]; **HMIS**: US Hazardous Materials Identification System (Health / Flammability / Physical hazard), from 0 (no hazard) to 4 (serious hazard). [NFPA-HMIS]

[18] US Federal hazards regulatory restrictions (Fire / Pressure /Reactivity / Immediate Hazard / Delayed hazard)

3.2 The summary

To be written

4. Conclusion

To be written

References

[Battistin]
1. M.Battistin, S.Ilie, R.Setnescu, B. Teissandier "Chemical and radiolytical characterization of some perfluorocarbon fluids used as coolants for LHC experiments", Part 1 (Chemical Characterization) TS-Note-2006-010, EDMS 804849 ;
2. Ibid, Part 2 (Radiolytical characterization) TS-Note-2007-005, EDMS 642110
3. M. Battistin, Technical Specification for the Supply of Perfluorocarbon fluids C3F8 and C6F14 for ATLAS, CMS and LHCb cooling systems, April 2010, CERN EN-CV, EDMS 10595763

[CERN GHG]

[CO2-AC]

[Kaiser]

1. Private communication, March 2016

[PoolBoiling]

1. Abundant literature is available on that topic (keywords for web search: "pool boiling" "Novec", "HFE" "dielectric")
2. BitFury
3. 3M-SGI-Intel – high-density cooling for super data centers
4. Allied Control – the pioneers of pool-boiling cooling for data centers

[HC]
1. Paratherm™ CR
2. Dynalene™ MV
3. Dowtherm ™ J

[PAO]
1. Dynalene™ HF-LO
2. See also [Tuma 2009]

[SE] Coolanol™ 20, 25R

[PFC]
1. 3M Fluoroinert™ Electronic Liquid FC-72[19], Product Information
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[FOM]

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[NFPA-HMIS]

NFPA: US National Fire Protection Association rating (Health / Flammability / Reactivity / Special hazards), from 0 (none) to 4 (danger). NFPA codes

Health=3 (warning) means: Corrosive or toxic. Avoid skin contact or inhalation; Flammability =1 (some caution) means: Combustible if heated; Reactivity=1 (Caution) means : May react if heated or mixed with water but not violently.

HMIS: US Hazardous Materials Identification System (Health / Flammability / Physical hazard), from 0 (no hazard) to 4 (serious hazard). HMIS codes

Health = 1 means: 1. Irritation or minor reversible injury possible; Flammability =1 means: Materials that must be preheated to above 93C before ignition will occur; Physical=1 means: Materials that are normally stable but can become unstable (self-react) at high temperatures and pressures. Materials may react non-violently with water or undergo hazardous polymerization in the absence of inhibitors.

Appendix A: Figures of Merit (FOMs)

Under certain assumptions, many thermal and hydraulic characteristics can be expressed as

$$M(a, b, c, d, e, L, D, \ldots) = (\rho^a k^b c_p^c \mu^d) \; v^e \; \Phi(L, D, \ldots) \tag{1}$$

where ρ, k, c_p and μ represent the density, thermal conductivity, specific heat (for constant pressure) and dynamic viscosity of the fluid, v stands for the fluid velocity, while the function $\Phi(L, D, \ldots)$ depends only on the system geometry and other design parameters unrelated to the fluid properties. The exponents a, b, c, d, e and the form of Φ-function depend on the heat transfer mode and the parameter being expressed. The FOMs become simple to compute:

$$r = \frac{M_1}{M_2} = \left(\frac{\rho_1}{\rho_2}\right)^a \left(\frac{k_1}{k_2}\right)^b \left(\frac{c_{p1}}{c_{p2}}\right)^c \left(\frac{\mu_1}{\mu_2}\right)^d \times \left(\frac{v_1}{v_2}\right)^e \tag{2}$$

The undefined ratio of velocities (v_1/v_2) is excluded by imposing additional constraints. This analytically simple approach is used in the present work and other similar studies, for example in [FOM.3-6]. It permits to construct a large variety of FOMs, with any kinds of constraints.

Assuming a widely used Dittus-Boelter equation for the Nusselt number Nu for a forced single-phase turbulent inner flow, the heat transfer coefficient (HTC) h can be expressed as follows:

$$h = Nu \left(\frac{k}{D}\right) = 0.023 \, Re^{4/5} Pr^{2/5} \left(\frac{k}{D}\right) = \rho^{4/5} k^{3/5} c_p^{2/5} \mu^{-2/5} v^{4/5} \times D^{-1/5} \sim Mo \; v^{4/5} \tag{3}$$

where Re, Pr and Mo are Reynolds, Prandtl and Mouromtseff [FOM.1] numbers defined as

$$Re = vD\rho/\mu = vD/\nu \tag{4.1}$$

$$Pr = c_p \mu / k \tag{4.2}$$

$$Mo = \rho^{4/5} k^{3/5} c_p^{2/5} \mu^{-2/5} \tag{4.3}$$

and $\nu = \mu/\rho$ is the kinematic viscosity.

The pressure drop Δp can be calculated using the Darcy-Weisbach equation

$$\Delta p = f_D \frac{\rho v^2}{2} \left(\frac{L}{D}\right) \tag{5}$$

in which the Darcy friction factor f_D in the simple case of a turbulent flow through smooth pipes is approximated as $f_D = 0.3164/Re^{1/4}$ (the Blasius equation, valid for $4000 < Re < 10^5$ [FOM.8]). With this, the Δp and the pumping power P can be expressed as

$$\Delta p = 0.1582 \, L \, D^{-5/4} \rho^{3/4} \mu^{1/4} v^{7/4} \sim \rho \nu^{1/4} v^{7/4} \qquad \text{and}$$

$$\eta P = \dot{V} \Delta p = S v \Delta p = 0.03955 \pi \, D^{3/4} L \rho^{3/4} \mu^{1/4} v^{11/4} \sim \rho \nu^{1/4} v^{11/4} \tag{6}$$

where $\dot{V}$ is the volume flow and η is the pump efficiency. Other interesting parameters are the temperature drops Δt and ΔT in the coolant across and along the pipe, respectively, which depend on the heat flow density q through the pipe and the overall heat load $\dot{Q}$[20]:

$$\Delta t = q/h; \quad \dot{Q} = \dot{m} \, c_p \, \Delta T = \dot{V} \rho c_p \, \Delta T \sim \rho c_p \, \Delta T \, v; \quad \Delta T \sim \dot{Q}/\rho c_p \, v \tag{7}$$

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[20] $\dot{Q} = S \int_0^L q(l) dl$. If the heat flow density is constant along the pipe, $\dot{Q} = SLq$.

Usually, $\dot{Q}$ is a fixed system parameter, as it largely depends on the thermal insulation and the difference of the temperatures inside and outside of the insulation.

The Yeh-Chu number $c_p h/P$ can be used to evaluate the aggregate thermal and hydraulic performance of a system [FOM.2–3]. It was suggested to express the desire to maximize the heat storage (c_p) and heat removal (h) capabilities, while at the same time minimizing the required pumping power (P). Using (3) and (6), we obtain

$$X = c_p h/P \sim \rho^{0.05} k^{0.6} c_p^{1.4} \mu^{-0.65} v^{-1.95} = \rho^{-0.6} k^{0.6} c_p^{1.4} v^{-0.65} v^{-1.95} \qquad (8)$$

We note that all equations (3), (5)–(8) have the desired form (1) and can be used to construct FOMs of the form (2).

Various system "constraints" or "conditions" can be used to eliminate the (v_1/v_2) term from (2):

- Constant fluid speed basis , $v_1 = v_2$, the simplest and most often used condition,

$$\left(\frac{v_1}{v_2}\right)_v = 1 \qquad (9)$$

- Constant pumping power basis. From (6), $\rho_1^{3/4} \mu_1^{1/4} v_1^{11/4} = \rho_2^{3/4} \mu_2^{1/4} v_2^{11/4}$ and

$$\left(\frac{v_1}{v_2}\right)_P = \left(\frac{\rho_1}{\rho_2}\right)^{-3/11} \left(\frac{\mu_1}{\mu_2}\right)^{-1/11} \qquad (10)$$

- Constant ΔT and $\dot{Q}$ basis. From (7), $\rho_1 c_{p_1} v_1 = \rho_2 c_{p_2} v_2$ and

$$\left(\frac{v_1}{v_2}\right)_{\Delta T} = \left(\frac{\rho_1}{\rho_2}\right)^{-1} \left(\frac{c_{p_1}}{c_{p_2}}\right)^{-1} \qquad (11)$$

Using (9)–(11), we can construct the following FOMs, meaningful for the SiPM application:

- r_{hv}, the ratio of HTCs, for the comparison with the same flow velocity. From (3), (7) and (9):

$$r_{hv} = \left(\frac{h_1}{h_2}\right)_{v=const} = \frac{\Delta t_2}{\Delta t_1} = \frac{Mo_1}{Mo_2} = \left(\frac{\rho_1}{\rho_2}\right)^{4/5} \left(\frac{k_1}{k_2}\right)^{3/5} \left(\frac{c_{p1}}{c_{p2}}\right)^{2/5} \left(\frac{\mu_1}{\mu_2}\right)^{-2/5} \qquad (12)$$

- $r_{\Delta pv}$, the ratio of pressure drops Δp, for the same flow velocity. From (6) and (9):

$$r_{\Delta pv} = \left(\frac{\Delta p_1}{\Delta p_2}\right)_{v=const} = \left(\frac{\rho_1}{\rho_2}\right)^{3/4} \left(\frac{\mu_1}{\mu_2}\right)^{1/4} = \left(\frac{\rho_1}{\rho_2}\right) \left(\frac{v_1}{v_2}\right)^{1/4} \qquad (13)$$

- r_{hP}, the ratio of HTCs, for the constant pumping power comparison, with v_1/v_2 determined from the $P_1 = P_2$. From (3) and (10):

$$r_{hP} = \left(\frac{h_1}{h_2}\right)_{P=const} = \left(\frac{\rho_1}{\rho_2}\right)^{32/55} \left(\frac{k_1}{k_2}\right)^{3/5} \left(\frac{c_{p1}}{c_{p2}}\right)^{2/5} \left(\frac{\mu_1}{\mu_2}\right)^{-26/55} \qquad (14)$$

- $r_{h\Delta T}$, the ratio of HTCs, for a fixed temperature drop along the pipe, ΔT, with v_1/v_2 determined from the $\Delta T_1 = \Delta T_2$. From (3) and (11):

$$r_{h\Delta T} = \left(\frac{h_1}{h_2}\right)_{\Delta T=const} = \left(\frac{k_1}{k_2}\right)^{3/5} \left(\frac{c_{p1}}{c_{p2}}\right)^{-2/5} \left(\frac{\mu_1}{\mu_2}\right)^{-2/5} \qquad (15)$$

- $r_{P\Delta T}$, the ratio of pumping powers, for a fixed temperature drop along the pipe, ΔT. From (6) and (11):

$$r_{P\Delta T} = \left(\frac{P_1}{P_2}\right)_{\Delta T=const} = \left(\frac{\rho_1}{\rho_2}\right)^{-2} \left(\frac{c_{p1}}{c_{p2}}\right)^{-11/4} \left(\frac{\mu_1}{\mu_2}\right)^{1/4} \tag{16}$$

- $r_{x\Delta T}$, the ratio of Yeh-Chu numbers (8), for a fixed temperature drop along the pipe, ΔT. From (8) and (11):

$$r_{x\Delta T} = \left(\frac{X_1}{X_2}\right)_{\Delta T=const} = \left(\frac{\rho_1}{\rho_2}\right)^{2} \left(\frac{k_1}{k_2}\right)^{0.6} \left(\frac{c_{p1}}{c_{p2}}\right)^{3.35} \left(\frac{\mu_1}{\mu_2}\right)^{-0.65} \tag{17}$$

The FOMs related to pressure drop and pumping power are of "the smaller, the better" type, while all other FOMs above are of "the greater, the better" type.

Table xx summarizes the values of the exponents for computing different FOMs.

It is worth noticing that the ratos of system performance parameters can be constructed using full-fledged correlations and parametrizations, like Gnielinski's correlation for Nu [FOM.7] and, say, Haaland's parametrization for f_D[FOM.8]. The resulting FOMs at a fixed fluid velocity are easy to compute. However, imposing other conditions (like $\Delta T_1 = \Delta T_2$) becomes non-trivial in that case.

Table A1 Numerical values of exponents in different FOMs (for dynamic viscosity)

	ρ	k	c_p	μ
r_{hv}	4/5 (0.8)	3/5 (0.6)	2/5 (0.4)	–2/5 (–0.4)
$r_{\Delta pv}$	3/4 (0.75)			1/4 (0.25)
r_{hP}	32/55 (0.582)	3/5 (0.6)	2/5 (0.4)	–26/55 (–0.473)
$r_{h\Delta T}$		3/5 (0.6)	–2/5 (–0.4)	–2/5 (–0.4)
$r_{P\Delta T}$	–2		–11/4 (–1.75)	1/4 (0.25)
$r_{x\Delta T}$	2	3/5 (0.6)	67/20 (3.35)	–13/20 (–0.65)

Table A2 Numerical values of exponents in different FOMs (for kinematic viscosity)

	ρ	k	c_p	ν
r_{hv}	2/5 (0.4)	3/5 (0.6)	2/5 (0.4)	–2/5 (–0.4)
$r_{\Delta pv}$	1			1/4 (0.25)
r_{hP}	6/55(0.109)	3/5 (0.6)	2/5 (0.4)	–26/55 (–0.473)
$r_{h\Delta T}$		3/5 (0.6)	–2/5 (–0.4)	–2/5 (–0.4)
$r_{P\Delta T}$	7/4 (1.75)		–11/4 (–1.75)	1/4 (0.25)
$r_{x\Delta T}$	7/20 (0.35)	3/5 (0.6)	67/20 (3.35)	–13/20 (–0.65)