CERN
CH1211 Geneva 23
Switzerland

Engineering Department

EDMS NO.	REV.	VALIDITY
1489771	**1.1**	**draft**

REFERENCE
WP-C6K-2015-Annex 1

Date: 2015-03-27

WORK PACKAGE:

Alternative to liquid perfluorocarbon C6F14 for mono-phase detector cooling applications at CERN

Annex 1: Commentaries to C6K validation tasks

Abstract

This document contains commentaries for the research tasks outlined in the main Work Package document. They represent an introduction for possible subcontractors and are complementary to the corresponding contracts.

DOCUMENT PREPARED BY:	DOCUMENT TO BE CHECKED BY:	DOCUMENT TO BE APPROVED BY:
Petr Gorbounov (PH-LBO)	Michele Battistin (EN-CV-PJ) Eric Thomas (PH-LBO-DO) Olivier Crespo (EN-CV-DC)	Michele Battistin Eric Thomas

DISTRIBUTION LIST:

M.Taborelli, B.Teissandier, R.Setnescu, P.Gorbounov, M.Battistin, E.Thomas, O.Crespo, B. Kaiser (3M Switzerland)

HISTORY OF CHANGES

REV. NO.	DATE	PAGES	DESCRIPTIONS OF THE CHANGES
1.0	2015-03-24	10	First version of the separate Annex 1, formerly the Appendix 3 of the main WP document
1.1	2015-03-27	10	The tasks are numbered and better structured; the “instrumentation” task is given a higher priority

TABLE OF CONTENTS

1. Introduction

The WP (Sections 2 and 3) highlights the directions of the C6K validation for detector cooling applications at CERN. This Annex contains a more detailed description of the related tasks. It begins with a reference to a similar study of C6F14 performed earlier at CERN [1], then outlines the C6K specifics and, finally, breaks down the problem into a more isolated (though not always entirely independent) topics that can be considered as the tasks (essentially, *small R&D projects*) to be outsourced. We are interested in the practical outcome and do not impose the methodology which will up to subcontractor(s). However, the task reports should contain the details of the methods used. We expect that subcontractors will each take several related tasks, in order to reduce overheads. Ideally, the entire Stage 2 (radiation chemistry) should be performed in the same lab.

2. The guidance of the C6F14 validation study at CERN

This study [1] provided useful guidelines for the coolant validation and suggested the following aspects to focus on:

- The selection of the analysis methods and techniques. They can be similar or equivalent to those used for C6F14 study [10], like gas chromatography (GC), spectroscopy (IR, UV-Vis) or spectrometry (FTIR), ion-selective potentiometry, viscosimetry etc, but not limited to these. Additional analysis methods (NMR?) can be involved, if appropriate.
- Composition and rectification of as-provided fluids.
- On-line purification: finding efficient methods of on-line treatment of circulating coolant (fresh or irradiated), to remove detrimental products resulting from the processes within the cooling system and unrelated to radiation (intake of water and/or air, extraction of polluting impurities from the cooling system structures and so on) and "radiation-induced" ones. It is important to take into account the *typical working temperatures* of the coolant, which can be well below freezing: -40^{o}C… -70^{o}C.
- Material compatibility.

One of the main messages of the C6F14 study was: the coolant should be kept as *pure* as possible – from the moment of the system filling through the entire life cycle. The impurities will cause problems and eliminating the very cause of the threat is the best way to secure the coolant stability and the system safety and integrity! Therefore, to learn everything about *purification* (or "cleaning", or "filtering") of the coolant is the goal No. 1 of the validation studies.

The goal No. 2 is to acquire knowledge about all detrimental chemical and radiation-induced products that can develop in the coolant during its service and determine criteria to decide when the coolant should be recycled. This will define the choice of specific filters and the "quality controls" used during the fluid service. The C6F14 study recommends to monitor the acidity, the F-ion and the polymer contents; to use UV-Vis spectrophotometry for the on-line control; and activated carbon (AC), activated alumina (AA) and molecular sieves (MS) for on-line cleaning. The two principal impurities that were shown to impact the radiation resistance in the case of C6F14 were *water* and *oxygen*.

The goal No. 3 is the *material compatibility*. All available information on the compatibility of the coolant with organic and inorganic substances (metals, polymers, elastomers,

typical filtering materials, other fluids) has to be collected and compared with the list of materials in the cooling system. Critical missing information has to be obtained experimentally.

3. What is special about Novec 649 (C6K)?

In the case of C6K[1], the fact of its intrinsic chemical reactivity, due to by the presence of the carbonyl group in its molecule, prevents from copying the methods of the previous C6F14 study and adds more "dimensions" to the fluid validation. The factors to consider here are:

1. Reactivity with liquid phase water by hydrolysis [2, 3] giving PFPrA and a volatile HFC compound (HFC 227ea).
2. Reported reactivity with the AA [4, section 2.6] which precludes their use as desiccants and fluoride adsorbers, recommended for C6F14. This requires a) to be verified and b) if confirmed, finding alternative methods of filtering of low-molecular-weight (LMW) impurities. In addition, this might limit the use of the gas chromatography (or require special selection of the stationary phase for C6K).
3. The carbonyl group in the molecule is not only the cause of (1) and (2), it facilitates the molecule scission by ionizing radiation and complicates the radiolytical reactions, by serving as a direct precursor to formation of such compounds as aldehydes, carbonyl acids and the very toxic *carbonyl fluoride CF2O* in the final state. CF2O was also detected among radiolysis products of C6F14, in presence of oxygen and water, but one can speculate that in C6K fluoroketone its yield might be higher. This is alarming because the water content (to hydrolize CF2O and remove it "naturally") in C6K will be limited by the proper hydrolysis and the energetic online drying, while the use of conventional AA filters might be precluded by the (2) above.
4. The carbonyl group in the C6K molecule will probably reduce the usefulness of the UV-Vis spectrometry for the online monitoring by enhancing the background in the interesting part of the spectrum (tbc).

4. The proposed scenario of C6K validation

The study, by analogy with the C6F14 project [1], can be split in two major stages: the *chemical* and the *radiolytical* characterization. Given the higher priority of low radiation-dose applications (SciFi, BGV, ATLAS Thermosyphon), the chemical characterization (the Stage 1) is more important at the moment. The main deliverables here are the "as-provided" *C6K composition*, *initial rectification* (if needed), *dedicated methods of C6K drying, PFPrA detection and removal* – within the entire working temperature range between +40°C and -70°C.

Preparation for the radiolytical study can begin in parallel with the Stage 1or be delayed, depending on the availability of the corresponding laboratory resources. The instrumentation for the post-irradiation analysis can be prepared and calibrated with the original fluid by adding controlled amounts of expected contaminants to it. The same applies to a development of on-line degassing (O2, CO2) and removal/neutralization of LMW by-products (CF2O, HF) at low temperatures.

[1] Ref. [12] contains the comprehensive review of literature about this fluid.

Radiolytical characterization (the Stage 2) is of primary importance for the wider range of cooling applications, involving the service in "hotter" areas (inner detectors, cables cooling). It will also be complementary to the low-dose application study by providing a deeper understanding of C6K-specific radiolysis mechanisms and more accurate evaluation of the expected radiation damage (with better known G-factors and yields of acids). This study can also be staged: we can start with pilot tests, irradiating a limited number of samples to a couple of representative doses, and proceed with further refined studies, e.g. with gamma and neutron irradiation and dedicated radiation-induced corrosion tests.

5. Stage 1 tasks (chemical characterization)

5.1. **Fluid Composition**. Selecting and testing the instrumentation (spectrometry, chromatography, NMR etc) to measure the composition of the coolant and identify impurities is more or less implicit to all tasks below and should unfold as part of the Stage 1. Ideally, it should converge by the moment when the radiolytical characterization (Stage 2) starts.

- An example of practical importance is FTIR spectrometry, as a possible technique for on-line monitoring of C6K impurities like HF, PFPrA, COF2 or water. Questions to be addressed: feasibility, choice of specific instrument, type of cells, range, sensitivity to particular impurities etc.

5.2. **Study of C6K samples**. Analyze the available C6K sample (3M™ Novec 649, purity 99.8% [5]). Particular stress should be on the nature of initial 0.2% impurities (its exact composition or at least the hydrogen content and boiling point). Obtain a sufficient quantity of rectified sample: 3-4 l for irradiations, with purity of ≥99.95%, as well as a sufficient quantity of ultra-pure sample for further chemical analyses (by distillation, degassing, filtration with AC etc)[2]. Evaluate a possibility (and necessity) of massive rectification of the coolant prior to service as coolant. Related task: 5.7 .

5.3. **C6K compatibility with materials**

- Help to interpret the outcome of the early tests (about 40 test vials of Novec fluids [9] with different water admixtures and immersed samples of different materials) launched in December 2014 [10].
- Study possible effects of PFPrA and C6K impurities (etching, deposits) on Titanium grade 5.
- Verify the expected miscibility and lack of chemical reactivity of C6K with PFCs, especially C3F8 (liquid phase) and C6F14. This is of interest because of a theoretical possibility of a contact between these fluids in the existing cooling systems.
- Evaluate the compatibility of C6F and other Novec fluids with several elastomers that are potentially usable in detector cooling circuits as flexible hoses, like ultra-pure plasticizer-free silicone rubbers (eg Tygon 2075, 2001) or PU rubbers (eg Tygotan C-555-A).

5.4. **Study of C6K hydrolysis.** The published data concerns mostly the hydrolysis of the gas phase in the atmosphere [2] or the uptake of a small amount

[2] As a last resort, an ultra-pure research grade fluid can be purchased, for chemical studies only.

of liquid C6K into water [3]. Our application deals with the bulk of C6K and a possible small intake of moisture. Questions to be addressed:

- what is the dynamics of water extraction from the liquid phase in direct contact with C6K, as function of T (between +40C and freezing point);
- is the water dissolved in C6K completely hydrolyzed, thereby prompting further extraction and posing no limit on the increase of acidity? Does it make sense to speak of the "water content" in the as-provided C6K[3]?
- Will C6K interact with solid water (ice, frost)?
- How the air (oxygen) dissolved in C6K affects the hydrolysis (if at all)?

5.5. **C6K drying methods.** Test the efficiency, capacity and stability of different classes of desiccants suitable for C6K. Information from 3M about C6K drying is only qualitative and somewhat contradictory: Ref. [4] claims that molecular sieves (MS) and silica gel (SG) "appear useful" for removing water from C6K", while [6] suggests avoiding MS and SG and using inorganic desiccants for C6K (anhydrous Ca and Mg sulfates… NaSO4?). In my opinion, another interesting and promising direction is to consider ion-exchange resins, e.g. DOWEX [7, p.7] for C6K drying. Activated Carbon?? Related task: 5.7 .

5.6. **Acids in C6K**.

- Select (or develop) the baseline *technique to detect acids* and measure the acid concentration in C6K - primarily sensitive to PFPrA, HF and, possibly, to a wider range of acids. Note that the method of [1, part 2, section 2.1.4] based on H2O extraction is hardly usable with C6K. Given the particular importance of early detection of the acidity build-up (as an indicator of an accidental water intake somewhere in the circulation loop), the stress should be on the *on-line acid detection in the wide temperature range*, from +40C down to -70C. Related task: 5.1
- Test the efficiency, capacity and stability of different classes of *acid removal methods* for C6K, for the range of acids that can be foreseen as hydrolysis and radiolysis products – HF, PFPrA, TFA etc. Among other methods, consider AC, carbon molecular sieves (CMS), ion-exchange resins (e.g. DOWEX M-43 for non-polar fluids [8]). Related task: 5.7

5.7. **Activated carbon filter and other filtering methods.**

Questions to be addressed:

- Which grade of AC is most efficient as a universal C6K purification filter (for the entire temperature range)?
- Are molecular sieves and membranes, in any possible form of this technique, applicable to C6K cleaning?;
- Same for ion-exchange resins (take into account the low working temperatures);

[3] The 3M Product Information [5a] quotes 20 ppm for water solubility in C6K. NB: the corresponding MSDS quotes "Nil" for C6K solubility in water.

6. Preparation for the Stage 2

6.1. **Gaseous impurities and evolutions**. Evaluate degassing techniques for C6K – to remove (O2, CO2, gaseous fluorides). Example: Ar or N2 purging, CMS.

6.2. **Special case: carbonyl fluride.** Propose and test a method of safe removal and neutralization of CF2O evolved from C6K. It would be nice to combine CF2O removal with extraction of other LMW impurities and gases (especially O2). Example: closed circuit purging with N2 inside the expansion tank, with on-line carbon molecular membrane to retain C6K and select CF2O as permeate and hydrolyze or adsorb it (eg with AA). Check if inline AC filter will be effective for extracting CF2O from the liquid phase (see below). Related task: 5.7

7. Stage 2 tasks (pilot radiolytical characterization)

At CERN:

7.1. **Fluid containers**. Manufacture, clean and fill the SS containers under controlled conditions, according to the following scheme:

- *Purified C6K* x 4 compositions (N,A,NW, AW) x 2 sets = 8 samples
  - N: argon (or N2) at 0.5 barG
  - A: dry air at 4 barG
  - NW: argon (or N2) at 0.5 barG + DI water (600 ppm)
  - AW: dry air at 0.5 barG + DI water (600 ppm)
- *As-received C6K* x 1 composition (AW) x 2 sets = 2 samples

Remarks: a) The two sets correspond to two irradiation doses;
b) Flat test strips (SS and/or Ti Grade 5, 180x10x1 mm3) in all containers (tbc);

At CERN or at the external facility:

7.2. **Irradiate all samples** with fast charged hadrons (e.g., at the CERN CHARM facility) to 50 Gy and 1000 Gy doses, representative for “low” and “medium” radiation environment application, taking into account the factor of “dilution” for the coolant [11] circulating between the irradiated and service zones. Penetrating gamma irradiation (e.g. with ^{60}Co or ^{137}Cs source) can be also used for the pilot test.

External radiation chemistry lab:

7.3. **Analyze the compositions** of the liquid and gas phases in all exposed samples and compare the results with the starting fluids compositions (related task: 5.1). Like in the C6F14 study [1], the contents of the following three classes of radiation-induced impurities have to be evaluated:

- High-molecular-weight pre-polymers soluble in C6K, insoluble polymers
- Acids and F-ions
- LMW products in gas and liquid phases: lower fluoroketones (including, and especially, CF2O), other fluorinated compounds, CO2. Also, for the gas phases: initial and final pressures; for the liquid phase: initial and final viscosities.

7.4. **Analyze test strips** surfaces (etching, composition of deposits)

7.5. **G-factors**. Estimate G(-M) and partial G-factors for C6K

7.6. ***The minimal analysis*** (in the case of limited resources) should focus on global features important for cooling: overall yield of aggressive acids (especially HF) and CFO2, the amount of residues in vacuum distillation of irradiated fluids, viscosity of irradiated fluids and their corrosiveness for different metals (titanium, SS, aluminum, brass, bronze).

Acronyms used in the Annex 1

AA – activated alumina

AC – activated carbon

CF2O – carbonyl fluoride, difluoroketone, fluorophosgene

CMS , CMM – carbon molecular Sieve, Membrane

HFC – hydrofluorocarbon

LMW – low-molecular-weight

MS – molecular sieve(s)

MM – molecular membrane(s)

PFC – perfluorocarbon(s)

PFPrA – perfluoropropionic acid, CAS 422-64-0

SS – stainless steel

SG – silica gel

TFA – trifluoroacetic acid

tbc – to be confirmed

References for the Annex 1

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 characterisation” TS-Note-2006-010, EDMS 804849
https://edms.cern.ch/file/804849/1/TS-Note-2006-010.pdf ;
Part 2: “Radiolysis effects in C6F14 fluids”, TS-Note-2007-005, EDMS 642110
https://edms.cern.ch/file/842110/1/TS-Note-2007-005.pdf

2. a) Taniguchi, N. et al. “Atmospheric chemistry of …” *J. of Phys. Chem. A*, 107(15), 2674-2679, 2003 http://pubs.acs.org/doi/pdf/10.1021/jp0220332
b) D. Jackson et al., “Atmospheric degradation of …”, Environ. SCi. Technol., 2011, 45(19), 8030-8036 http://pubs.acs.org/doi/pdf/10.1021/es104362g

3. NICNAS report No. STD/1019 “3M™ Novec™ Fire Protection Fluid 1230”
http://www.nicnas.gov.au/__data/assets/pdf_file/0011/10361/STD1019FR.pdf

4. P.E. Tuma, Fluoroketone C2F5C(O)CF(CF3)2 as a Heat Transfer Fluid for Passive and Pumped 2-Phase Applications, 24th SEMI-THERM Symposium, 2008
http://ieeexplore.ieee.org/stamp/stamp.jsp?arnumber=04509386

5. 3M Certificate of Analysis (Dec-09-2013, Stock Number 98-01212-3240-4), for the 17 kg batch of Novec 649 purchased by CERN from 3M Switzerland.

6. B. Kaiser (3M Switzerland, bkaiser@mmm.com) Private communication

7. DOWEX Ion Exchange Resins, Dow Liquid Separation Publications, http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0041/0901b80380041d4e.pdf?filepath=liquidseps/pdfs/noreg/177-01395.pdf&fromPage=GetDoc

8. DOWEX M-43 Ion Exchange Resin, Application Information, http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0030/0901b803800307e7.pdf?filepath=liquidseps/pdfs/noreg/177-01773.pdf&fromPage=GetDoc

9. P.Gorbounov, E. Thomas, M. Battistin, Comparison of liquid coolants suitable for single phase detector cooling, Internal Note, unpublished (EDMS …, temporarily in https://twiki.cern.ch/twiki/pub/LHCb/C6K/Coolants_review.pdf

10. P. Gorbounov, Pilot material compatibility tests for 3M Novec 549, 7100 and 7200 fluids , December 2014, Internal Memo, unpublished (EDMS …)

11. P.Gorbounov, Assessment of the radiation damage to the coolant in SciFi tracker, November 2014, EDMS 1421023 and https://twiki.cern.ch/twiki/pub/LHCb/C6K/Memo_on_irradiation_damage_for_C6K.pdf

12. P.Gorbounov, Project: 3M Novec 649 as a replacement of C6F14 in liquid cooling systems (the literature review), https://twiki.cern.ch/twiki/pub/LHCb/C6K/Novec_Memo.pdf