Caracterizarea fizico-chimica a unor perflurocarboni utilizati ca fluide de racire in LHC-CERN

I. Metode fizico-chimice de caracterizare

Diana Ilie[a,b], *Sorin Ilie*[b], *Radu Setnescu*[a,b,c]

[a] ICPE CA, Splaiul Unirii 313, Bucuresti, Romania
[b] CERN, CH 1211 Geneva 23, Elvetia
[c] Universitatea Valahia Targoviste, Bd Regele Carol No. 2 Targoviste, Romania

Physico-chemical characterization of some perfluorocarbon used as coolants for LHC experiments

Part one: Physico-chemical characterization methods

Part two: Radiation induced effects and purification

Diana Ilie[a,b], *Sorin Ilie*[b], *Radu Setnescu*[a,b,c]

[a] ICPE CA, Splaiul Unirii 313, Bucuresti, Romania

[b] CERN, CH 1211 Geneva 23, Elvetia

[c] Universitatea Valahia Targoviste, Bd Regele Carol No. 2 Targoviste, Romania

SUMMARY

- Perfluorocarbon fluids were characterized by applying different techniques: GC, FT-IR, UV-Vis, potentiometry, distillation, etc.

- The first aim of this work was the quality control, the identification and the quantification of different impurities which could increase the radiation sensitivity of these fluids.

- The procedures settled-up in this work are sensitive to the presence of disturbing impurities and were used for the analyses of the as received perfluorocarbons and for the irradiated fluids.

- The second aim of this work was to assess the radiation induced modifications on different fluids irradiated gamma Co 60: acidity (HF), polymer & pre-polymers, new molecules, etc.

- Cleaning tests were carried out on the as received fluids and on the irradiated ones to assess the efficiency of such purification treatments.

Introduction

Perfluorocarbons

Examples of CERN applications

Experimental

Materials

Studied fluids

Instruments and Methods

Gas chromatography

FT-IR spectroscopy

UV-vis spectroscopy

Potentiometry

Others

Results and discussion

Conclusions

Perfluorcarbons = compounds obtained or formally derived from the corresponding hydrocarbons by total H replacing by F atoms

- **saturated (perfluroalkans) e.g. CF_4, C_3F_8, C_6F_{12}**
- unsaturated (perfluoroalkenes...) e.g. C_2F_4, C_3F_6, C_4F_8
- aromatics e.g. C_6F_6, $C_6F_5CF_3$, $C_6F_5CF{=}CF_2$

Synthesis methods:

- Direct fluorination of the inferior alkanes $\rightarrow$ CF_4, C_2F_6, C_3F_8
- Fowler process:

$$2\ CoF_2 + F_2 \rightarrow CoF_3$$

$$C_6F_{14} + 28\ CoF_3 \rightarrow C_6F_{14} + 14\ HF$$

Applied for the synthesis of F2 Flutec products (ex. PP1)

- Simons process (HF electrolysis of a substrate dissolved in HF):

$$2N(C_6H_{13})_3 + 90\ HF \rightarrow 6\ C_6F_{14} + 2\ NF_3 + 45\ H_2$$

perfluoroamines result as by-products:

$$2N(C_6H_{13})_3 + 42\ HF \rightarrow 2N(C_6F_{13})_3 + 21\ H_2$$

Is applied for 3M Fluorinert (ex. PF 5060) perfluorocarbons synthesis (from amines or ethers)

Special category of compounds due to the exclusive presence of C and F atoms in molecule:

- chemical inertness (thermal, oxidative, or hydrolytic stability; no flammability, no corosivity..)
- low surface tension
- high density
- interesting rheological and tribological properties
- excellent dielectric properties (low dielectric constant, high resistivity)
- low otxicity or no toxic products
- high capacity of gases dissolving (O_2: 65 mL/100 mL liquid perfluorohexane)
- zero potential or low potential of ozone degradation

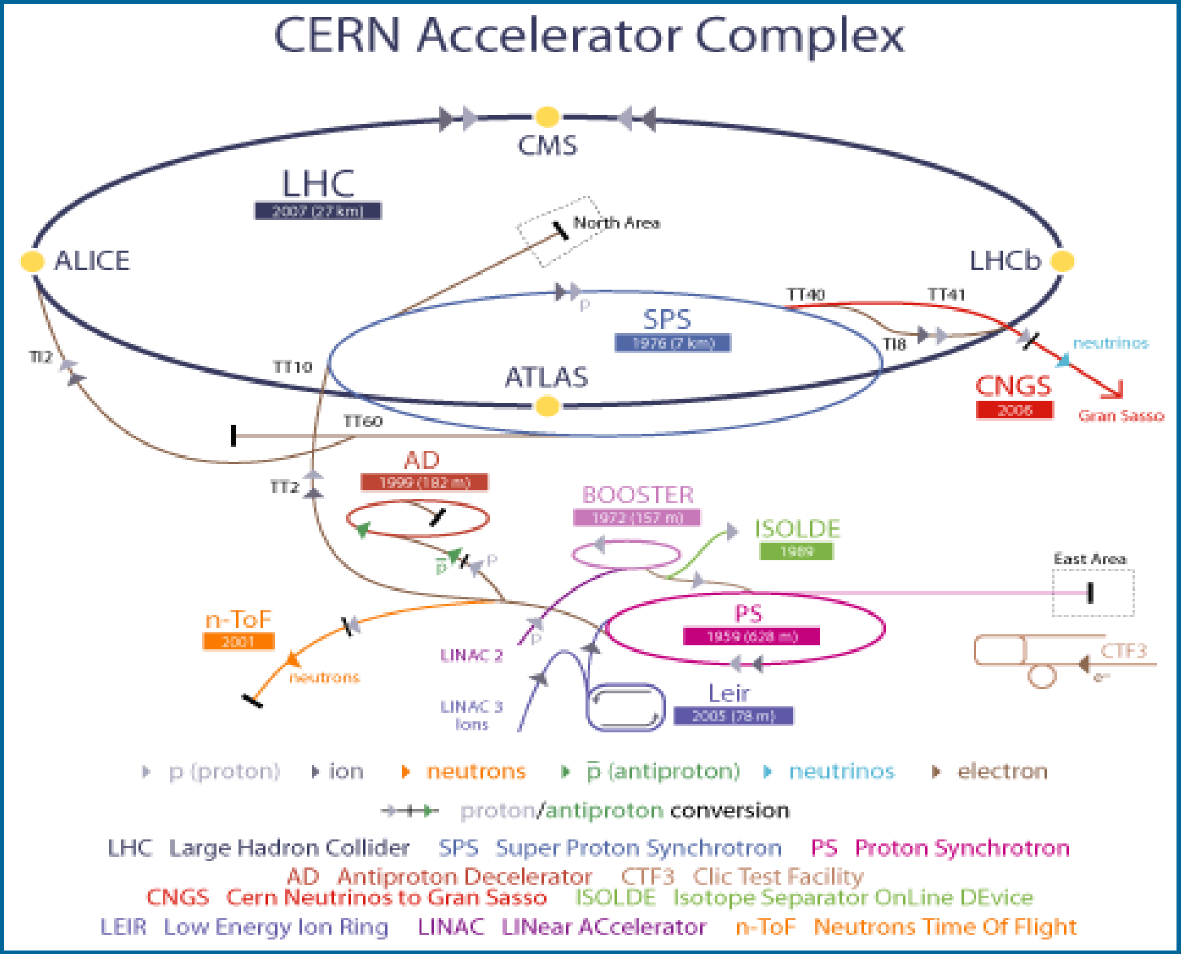
Structural characteristics

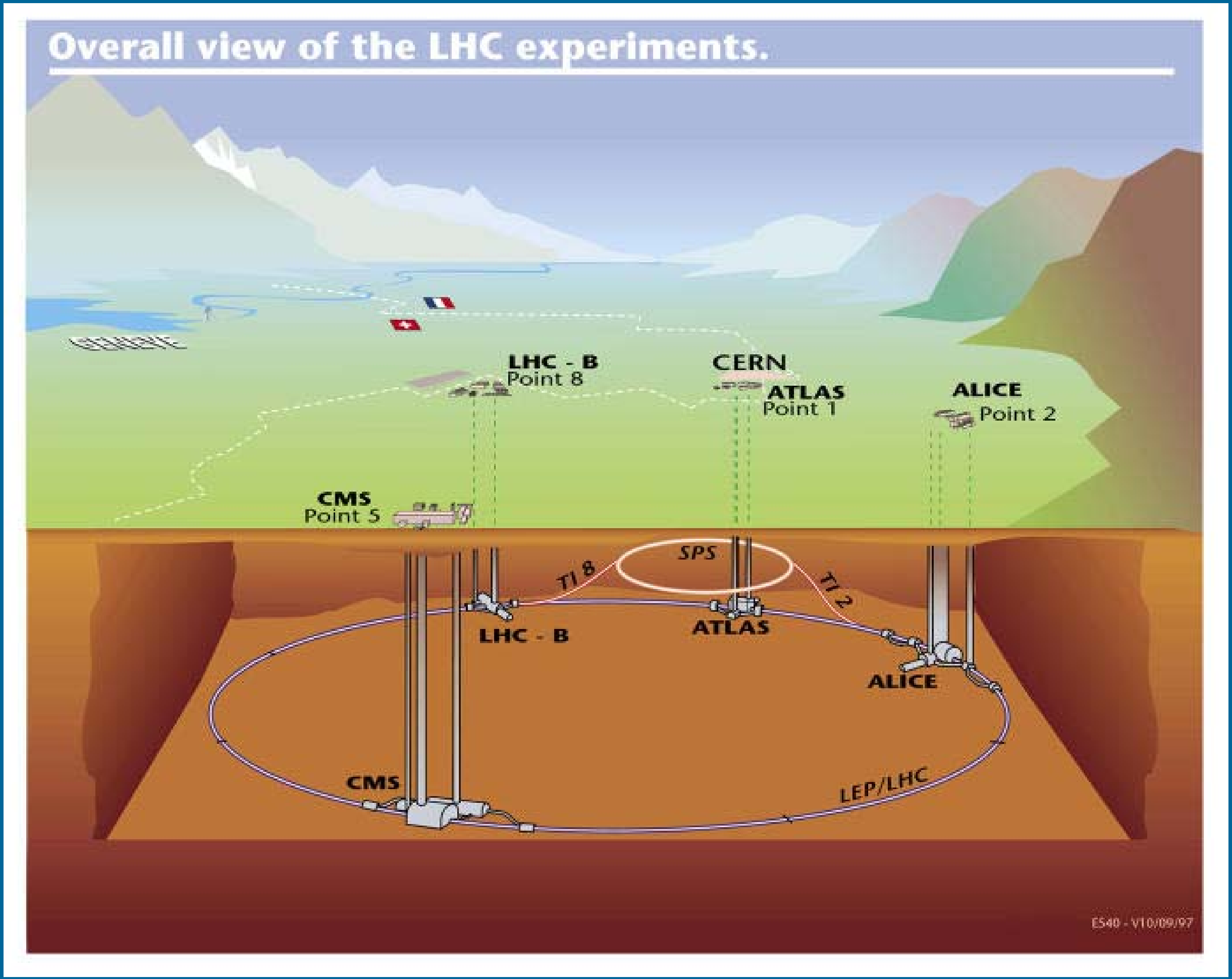
- high bond C-F energy: 540 kJ/mol; C-C 348 kJ/mol; C-H 413 kJ/mol
- bond length C-F: 1,32 Å; C-C; 1.54 Å; C-H 1.09 Å
- conformation of CF_2 segments: helix 15/7 at T> r.t. and 13/6 at T<r.t); in alkanes, the CH_2 segment conformation is zigzag, with C atoms in all-trans;

Applications

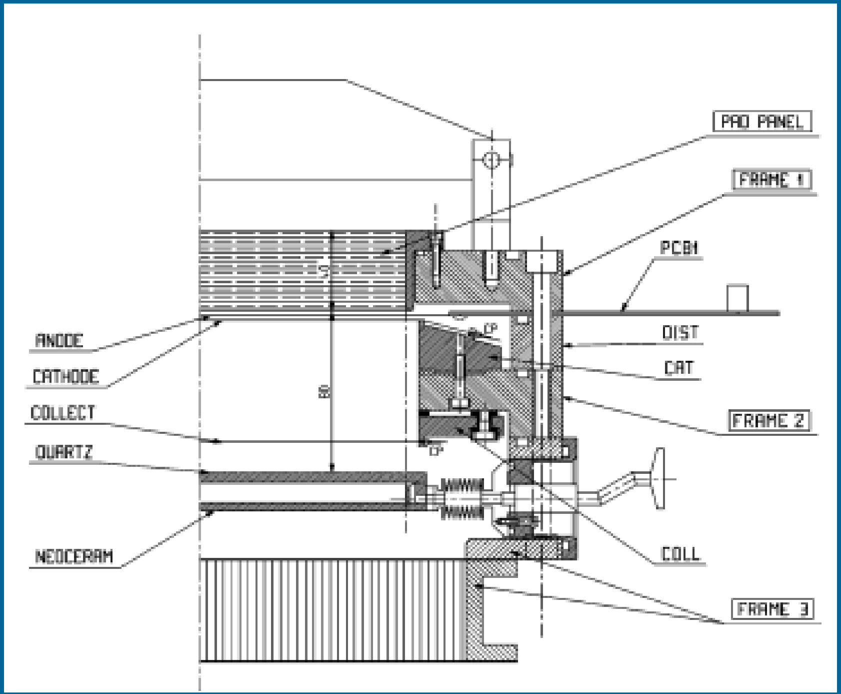
- Electronics, electrical engineering, other technical
  - liquid dielectrics (non inflammable, chemically stable, high dielectric strength) in electrical insulation of high voltage components;
  - cooling of electronic components by direct contact (immersion) or by heat transfer
  - surface cleaning (grease and particles removal)
  - volatile solvent for lubricant deposition
  - thermal shock testing (US MIL 883-1011)
  - gross leak detection (US MIL 883-1014)
  - manometric fluid
  - tracers for atmospheric tagging, petroleum reservoir mapping, building ventilation studies etc.
  - fire extinguishers
- Medical
  - artificial blood, liquid breathing
  - wound surgery (O_2 supply)
  - eye surgery
  - sterilization of surgical equipment
  - imaging (contrast imaging agent)
  - drug delivery
  - treatment of carbon monoxide poisoning

- Cosmetics

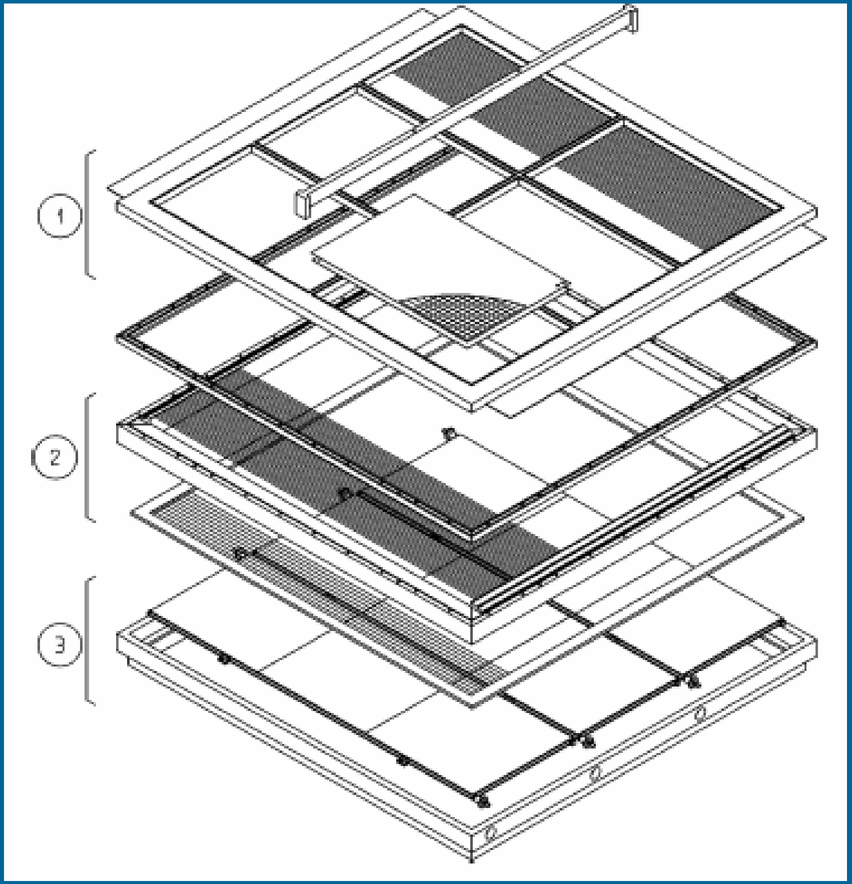

CERN Accelerator Complex
CMS
LHC
2007 (27 km)
North Area
ALICE
LHCb
TT40
TT41
SPS
1976 (7 km)
TI8
neutrinos
TI2
TT10
ATLAS
CNGS
2006
Gran Sasso
TT60
AD
1999 (182 m)
TT2
BOOSTER
1972 (157 m)
ISOLDE
1989
East Area
n-ToF
2001
PS
1959 (628 m)
LINAC 2
CTF3
neutrons
LINAC 3
Ions
Leir
2005 (78 m)
p (proton)
ion
neutrons
p̄ (antiproton)
neutrinos
electron
proton/antiproton conversion
LHC Large Hadron Collider
SPS Super Proton Synchrotron
PS Proton Synchrotron
AD Antiproton Decelerator
CTF3 Clic Test Facility
CNGS Cern Neutrinos to Gran Sasso
ISOLDE Isotope Separator OnLine DEvice
LEIR Low Energy Ion Ring
LINAC LINear ACcelerator
n-ToF Neutrons Time Of Flight


Overall view of the LHC experiments.
LHC - B
Point 8
CERN
ATLAS
Point 1
ALICE
Point 2
CMS
Point 5
SPS
TI 8
TI 2
LHC - B
ATLAS
ALICE
CMS
LEP/LHC
E540 - V10/09/97

CERN-LHC: part of the 27 km tunnel



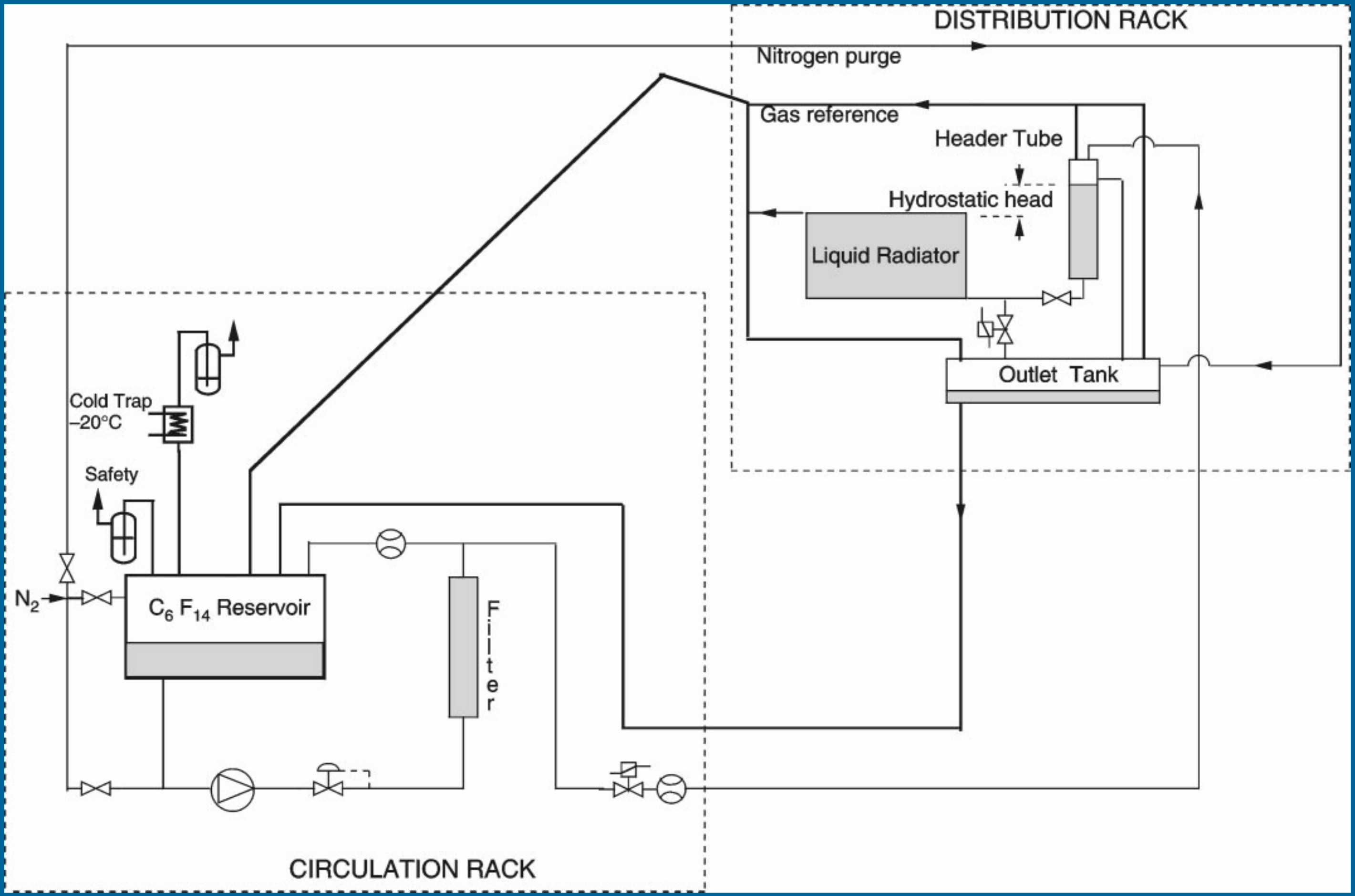
CERN-LHC/ALICE: Cross-section of the CsI-RICH prototype in a plane parallel to the anode wires.



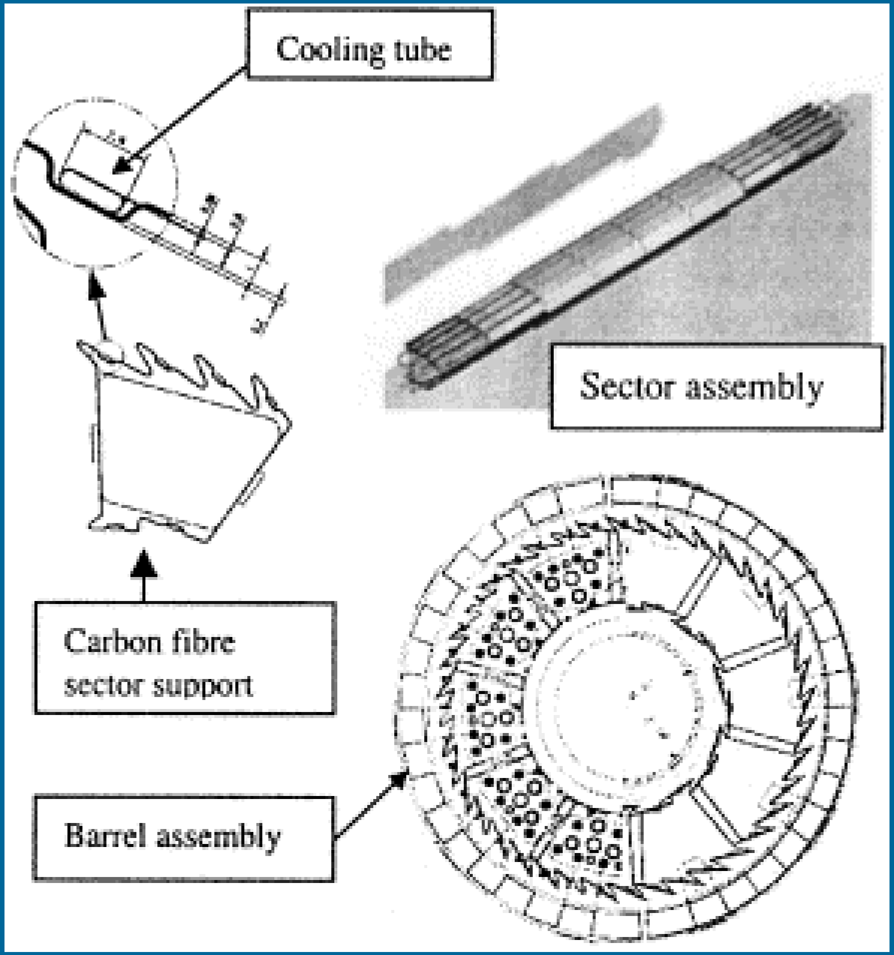
CERN-LHC/ALICE: isometric view of a HMPID module. (1), (2), (3) are the elements known as Frame-1, Frame-2, Frame-3, respectively.

CsI-RICH = Ring Imaging Cherenkov Detector based on CsI photoconverter

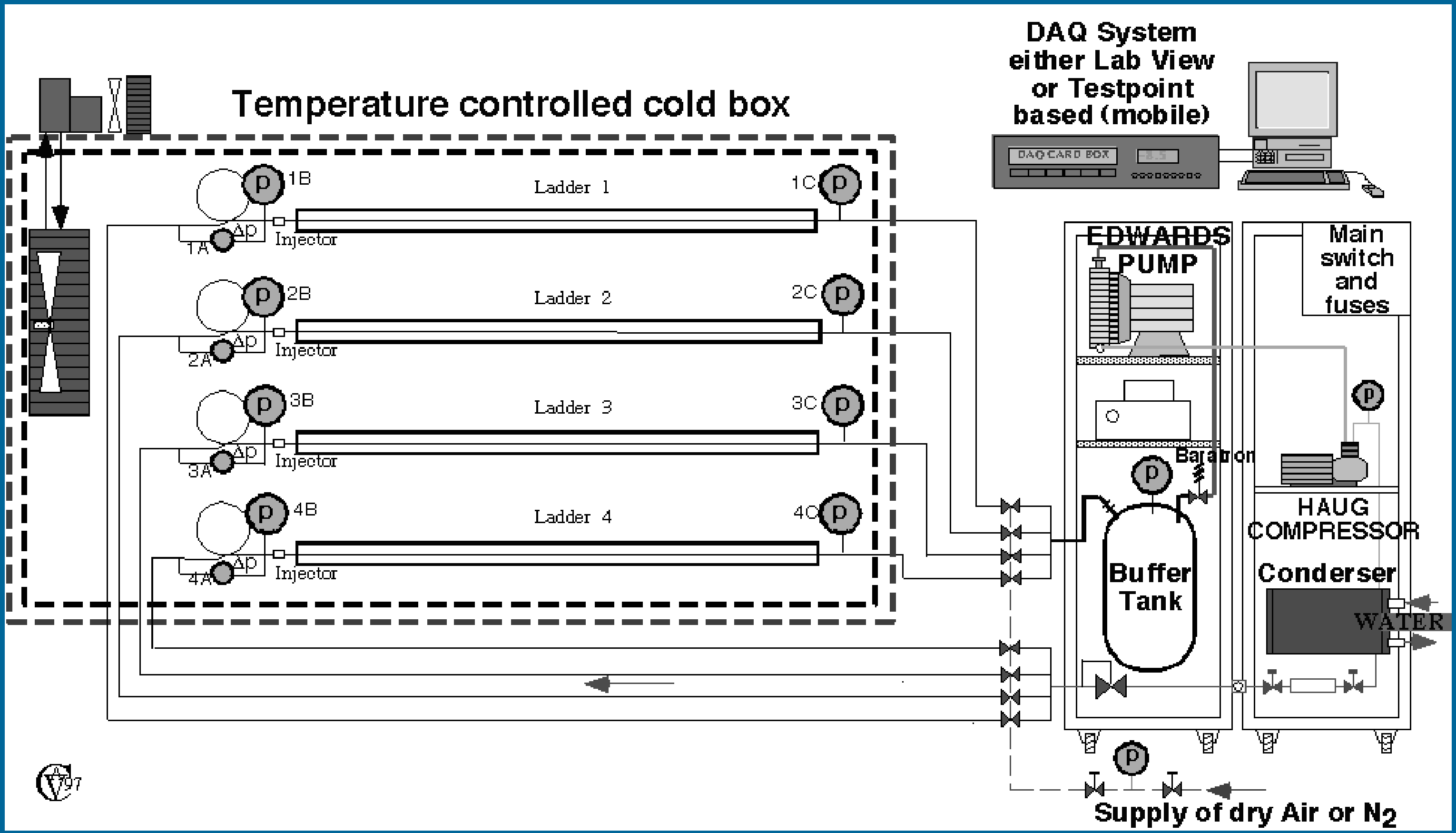
HMPID = High Momentum (1.5-5 GeV/c) Particle Identification Detector



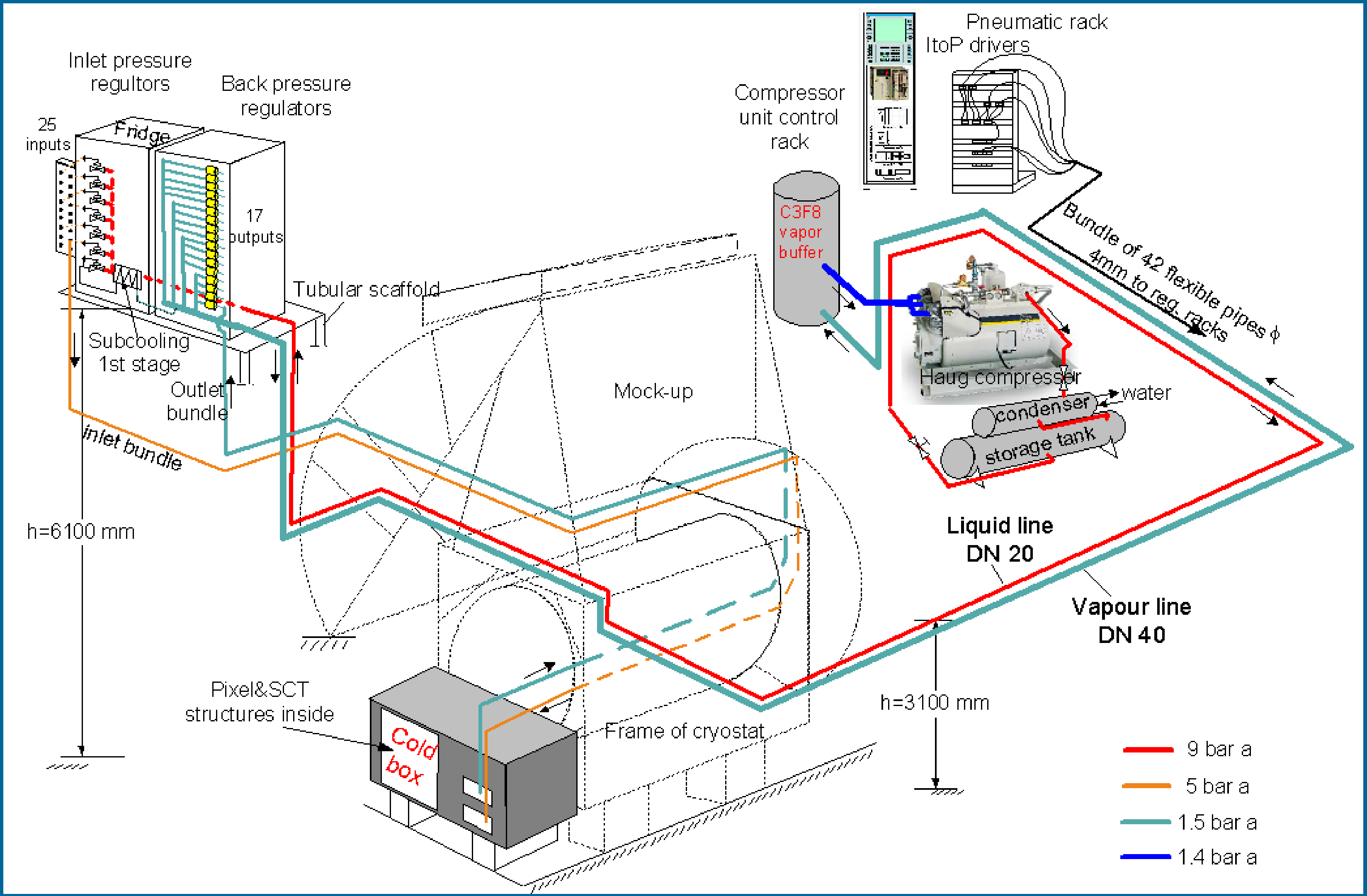
CERN-LHC/ALICE: Schematic of the C_6F_{14} circulation system



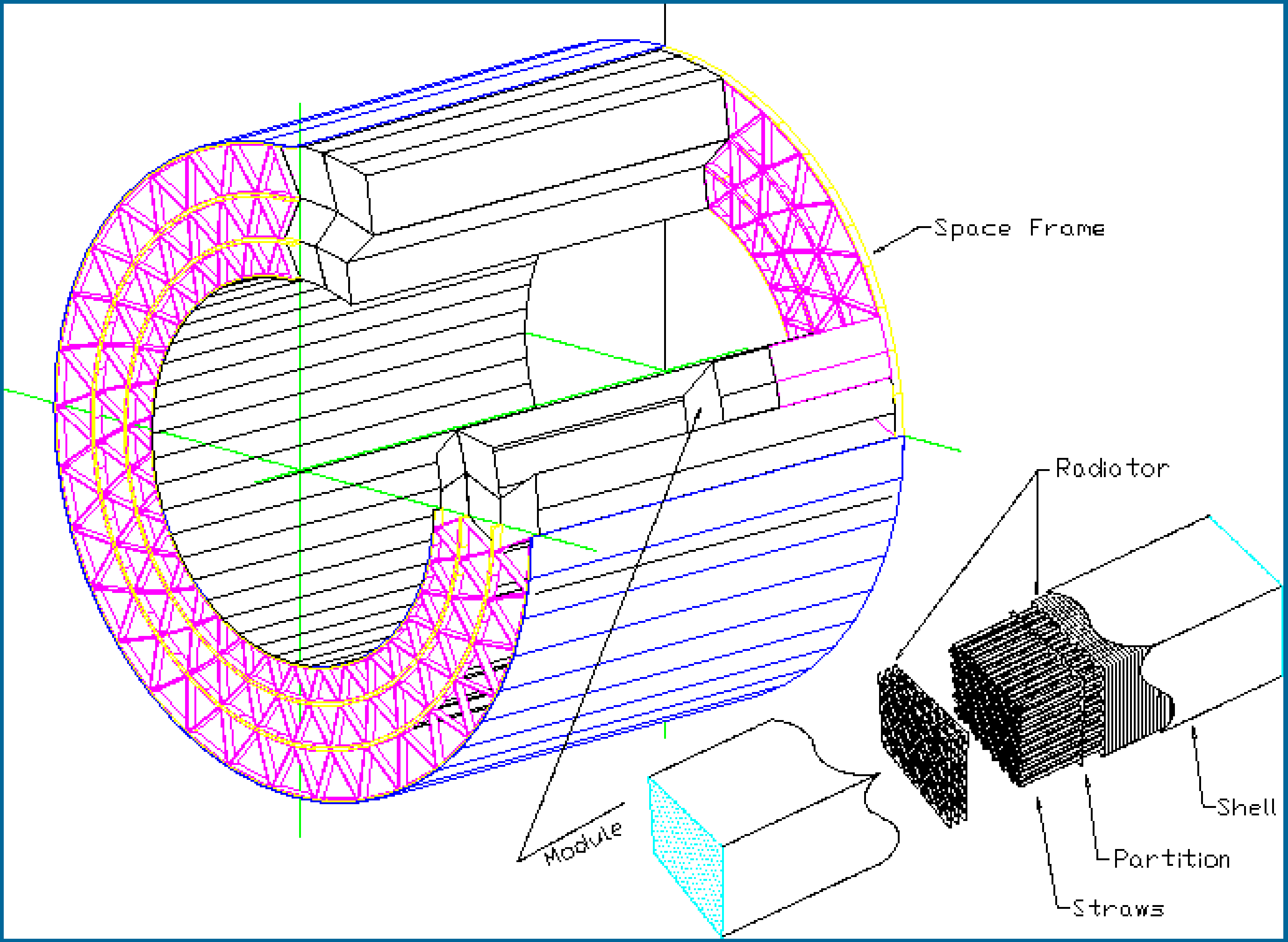
CERN-LHC/ALICE, pixel detector: sector assembly and detail of the cooling tube (C_6F_{14})



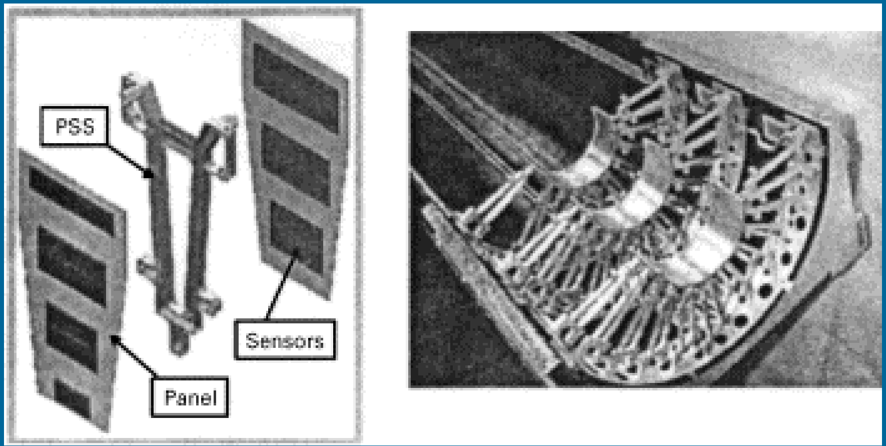
CERN - LHC/ATLAS: The Two-Stage Evaporative Recirculator (C_3F_8)

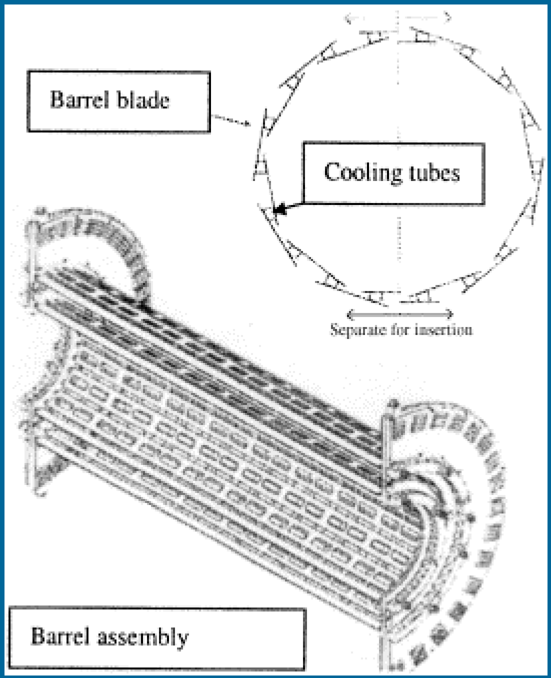


CERN-LHC/ATLAS: Schematic of the 6 kW Evaporative Cooling Recirculator(C_3F_8)

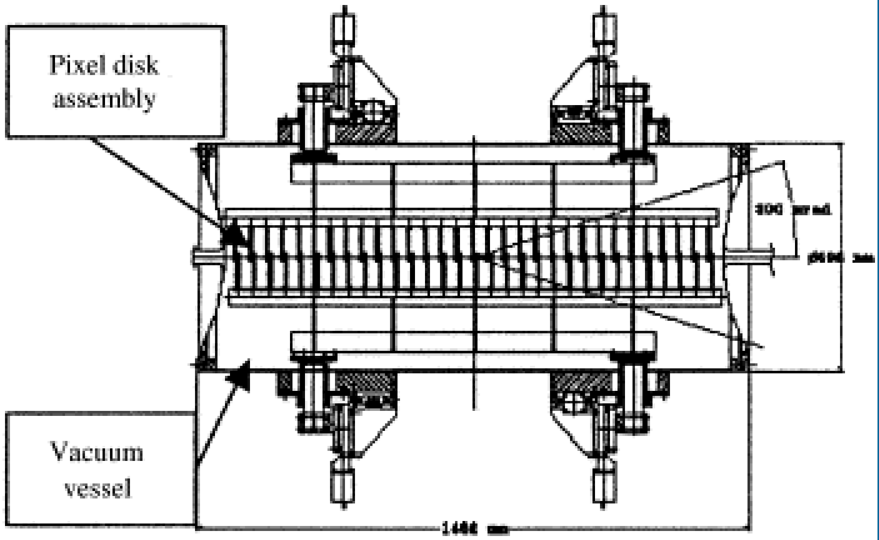


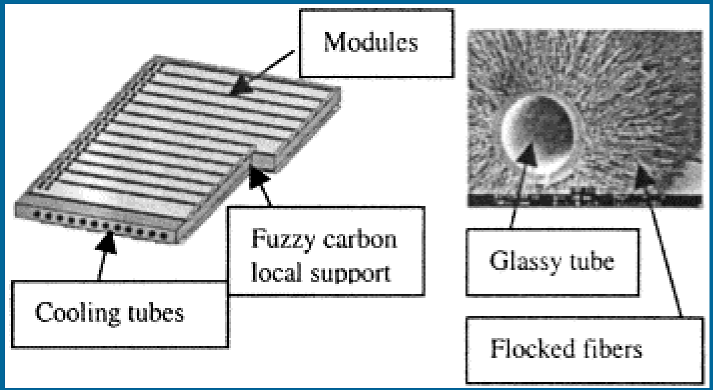
CERN-LHC/Atlas: Diagram of the barrel section of the TRT which is comprised of 96 individual modules, 32 each of three different sizes.





CERN-LHC/CMS: pixel detector (C_6F_{14})





CERN-LHC/CMS: BTeV detector (C_6F_{14})

Table 1 – Irradiation doses expected for cooling fluids in various LHC experiments

Experience	Detector	Fluid	2007 (Gy)	2008 (Gy)	2009 (Gy)	2010 (Gy)	2011 (Gy)	2012 (Gy)	2013 (Gy)	2014 (Gy)	2015 (Gy)	2016 (Gy)
ATLAS	SCT Evap.	C_3F_8	40	240	1240	5240	9240	1324 0	1724 0	2124 0	2524 0	2924 0
ATLAS	TRT	C_6F_{14}	3	18	118	418	718	1018	1318	1618	1918	2218
ATLAS	Cables	C_6F_{14}	1	6	28	126	226	326	426	526	626	726
CMS	Pixel	C_6F_{14}	480	980	1440	1920	2400	2880	3360	3840	4320	4800
CMS	Silicon Strips	C_6F_{14}	140	280	420	560	700	840	980	1120	1260	1400
LHCb	Inner Tracker	C_6F_{14}	7	40	73	106	139	223	306	389	472	556
LHCb	Trigger Tracker	C_6F_{14}	4	25	47	68	89	142	195	248	301	353
LHCb	RICH 1&2	C_6F_{14}	1	3	6	9	12	19	26	33	39	48

Experimental. Materials

The main perfluorocarbon fluids studied in this work

No.	Product name	Supplier	Composition	Name used in this report
1	PF 5060	3M Chemicals, USA	mainly n-C_6F_{14} (n-perfluorohexane)	PF 5060
2	PF 5060 "purified"	3M Chemicals, USA; tentatively " treated" (purified) in CERN Chemistry Laboratory	mainly n-C_6F_{14} (n-perfluorohexane)	purified PF 5060
3	PF 5060 DL	3M Chemicals, USA	mainly n-C_6F_{14} (n-perfluorohexane)	PF 5060 DL
4	Flutec PP1	F2 Chemicals Ltd., UK	mainly iso-C_6F_{14} (iso-perfluorohexane)	PP1
5	C_3F_8 (R218)	ASTOR, Russia	C_3F_8 perfluoropropane	C_3F_8 perfluoropropane

Experimental. Instruments and methods

Gas chromatography

GC-TCD Hewlett - Packard 5890

- Porapak Q packed column (4m, 1/8'')
- conditions:

C_3F_8:

- isothermal;
- oven temperature: 80 °C
- inlet temperature: 130 °C
- detector temperature: 140 °C
- carrier gas: He; flow 18 mL/min.
- loop: 0.25 mL

C_6F_{14}:

- T_1 = 140 °C/ 40 min. T_2 = 170 °C/ 20 min.; heating rate: 8 °C/min.
- inlet temperature: 140 °C
- detector heater: 180 °C
- carrier gas: He; flow 18 mL/min.
- injected volume: 2 - 10 μL

GC-MSD Agilent 6890 Series GC System with Agilent 5973 Mass Selective detector

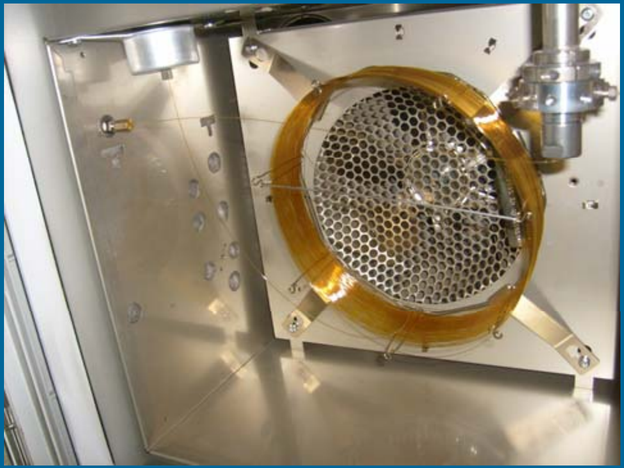
- **GasPro** capillary column (60 m)
- condtions

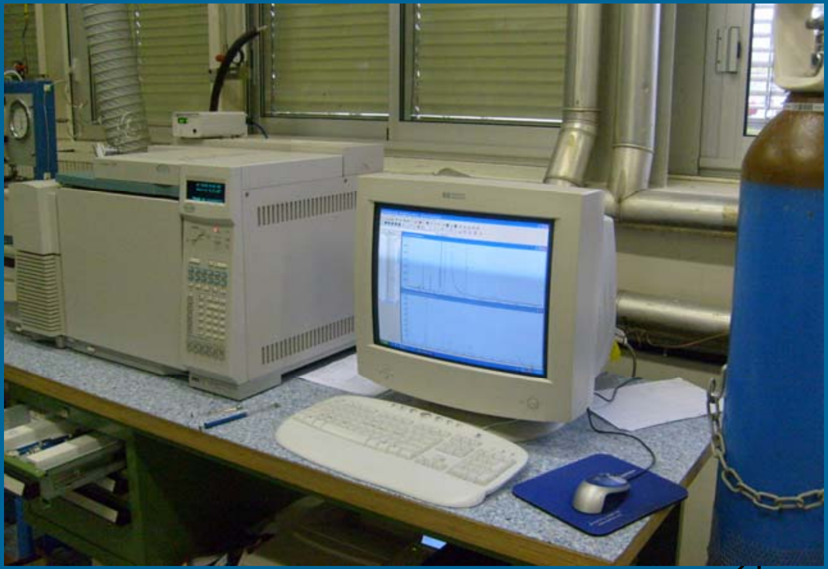
C_3F_8:

- T_1 = 90 °C/ 15 min. T_2 = 170 °C/ 10 min.; heating rate: 20 °C/min.
- detector temperature: 250 °C
- heater temperature: 260 °C
- split: 300:1
- carrier gas: He; flow 0.9 mL/min.
- loop: 0.25 mL

C_6F_{14}:

- T_1 = 120 °C/ 20 min. T_2 = 200 °C/ 10 min.; heating rate: 8 °C/min.
- detector temperature: 250 °C
- heater temperature: 260 °C
- injected volume: 2 - 10 μL
- split: 300:1
- carrier gas: He; flow 0.9 mL/min.





FT-IR spectroscopy

Bruker Vertex 70 FT-IR Spectrophotometer

Conditions:

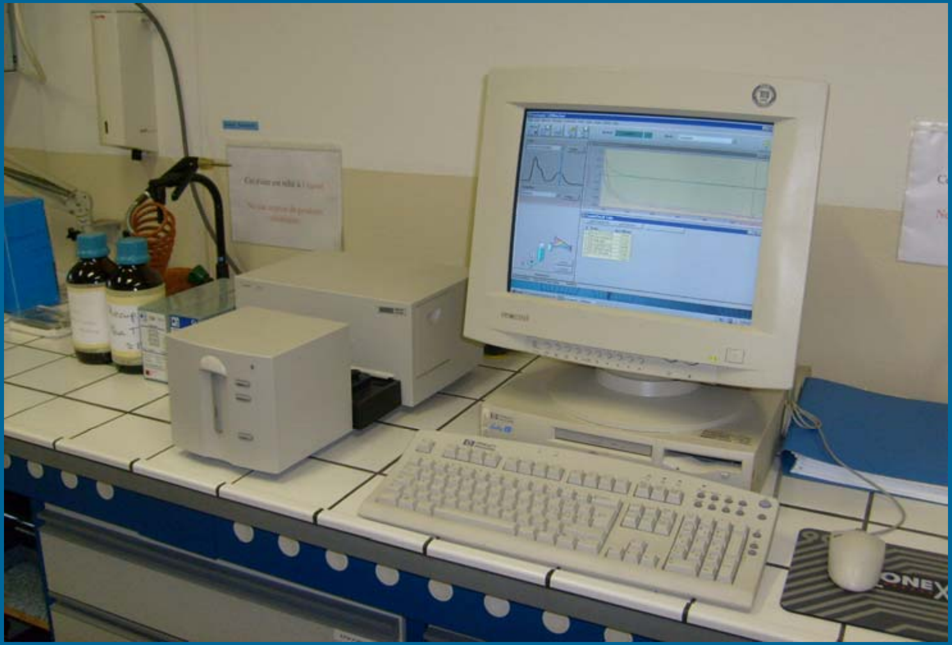
- Aperture: 6 mm;
- Resolution: 4 cm^{-1};
- Sample scan time: 32 scans
- ZnS cells (Cleatran); optical path length: 5 mm
- transmission or absorption mode

UV-vis spectrophotometry

Agilent 8453 spectrophotometer (single beam)

Conditions:

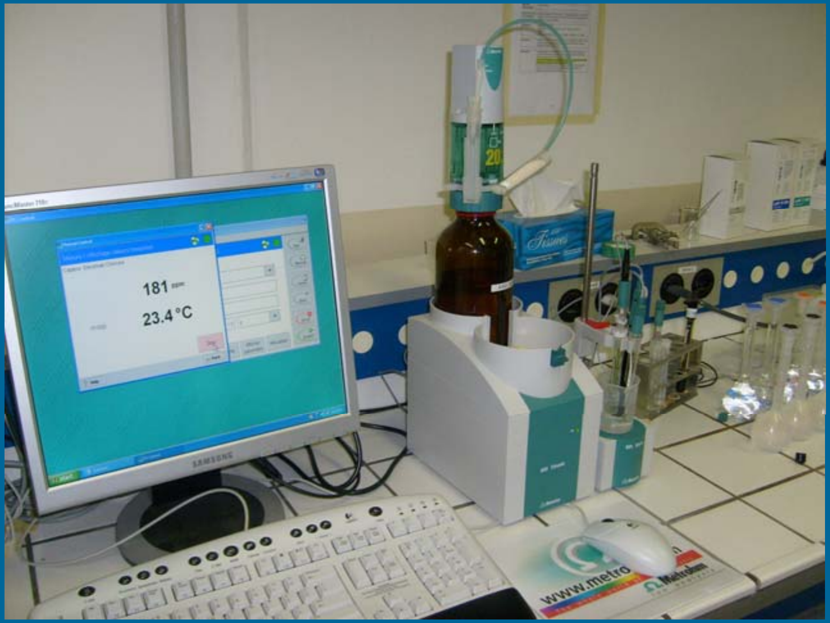
- Silica cells (optical path length: 1 cm)
- spectral range: 190 - 1100 nm

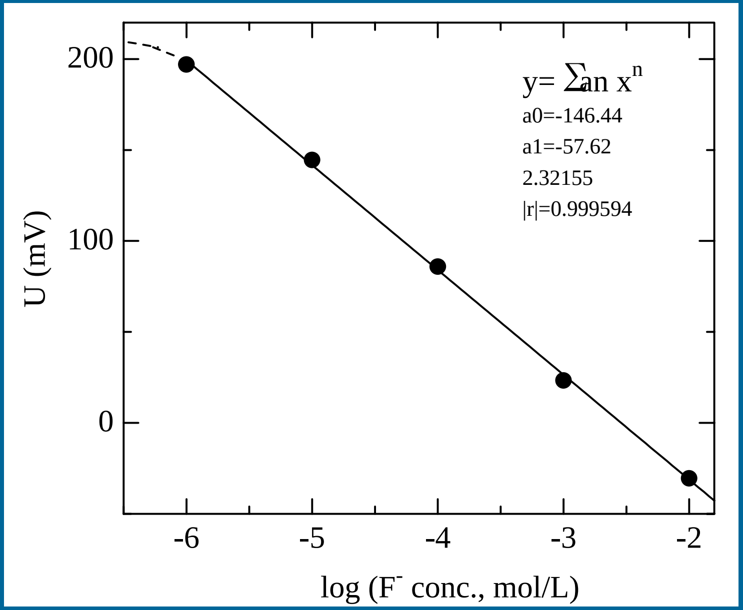


F^- dosation

Methrom Titrando 809 - potentiometric, F^- selective electrode

- reference electrod: Ag/AgCl (double junction, KCl solution 3 mol/L)
- calibration: NaF standard solution



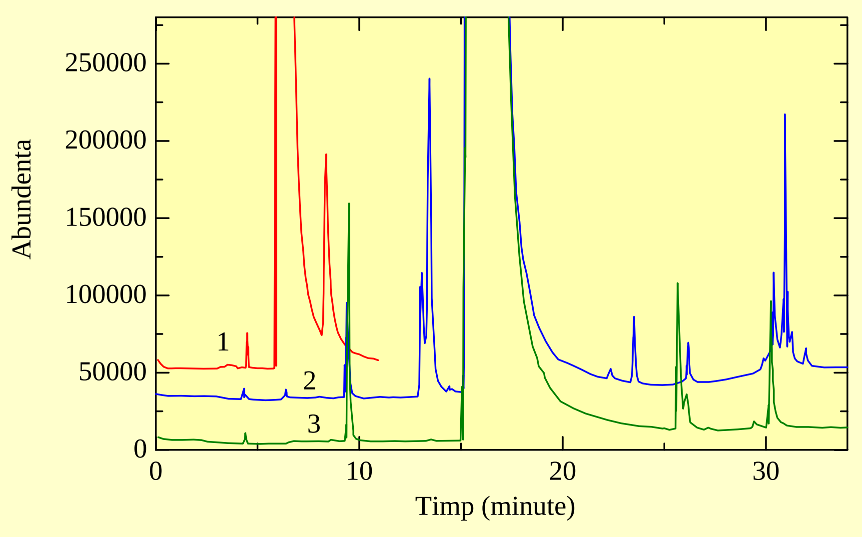


Calibration curve of F^- selective electrode potential as a function of F^- concentration

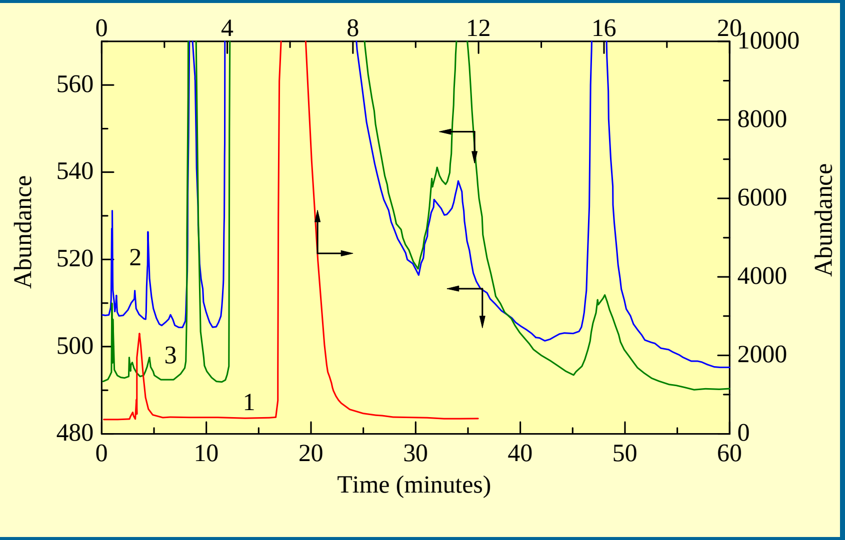
Results and discussion

- The purities of the received fluids were found to be higher as 98.5 %, conform to the CERN Technical Specification.

- The chemical nature of some impurities present in n-C6F14 was found to be different from that evidenced in iso-C_6F_{14}. The perfluorinated isomers and their homologous compounds, commonly present, are not foreseen to be detrimental to the behavior of the cooling fluids during irradiation.

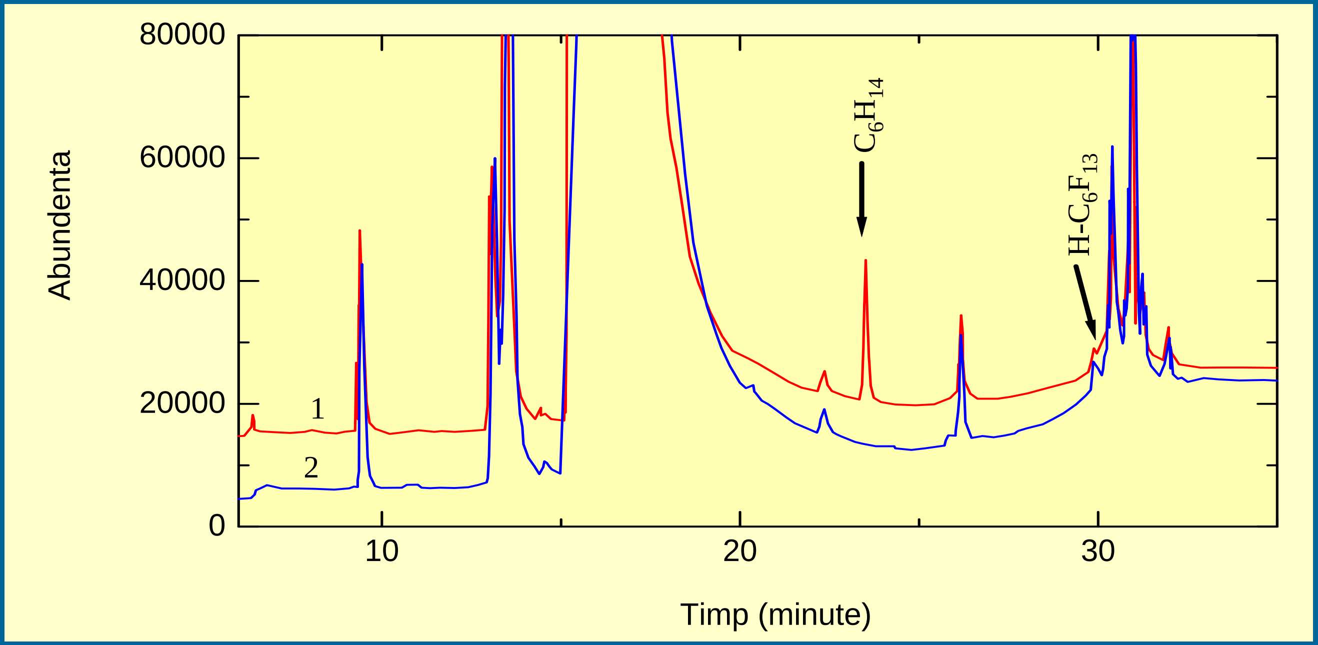


GC-MSD chromatograms for the studied perfluorocarbons: (1) C_3F_8; (2) n-C_6F_{14}; (3) iso-C_6F_{14}

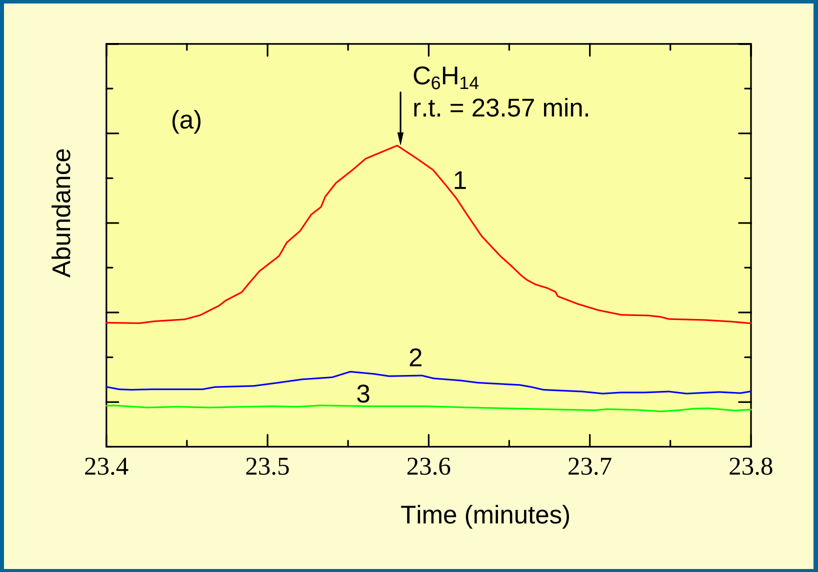


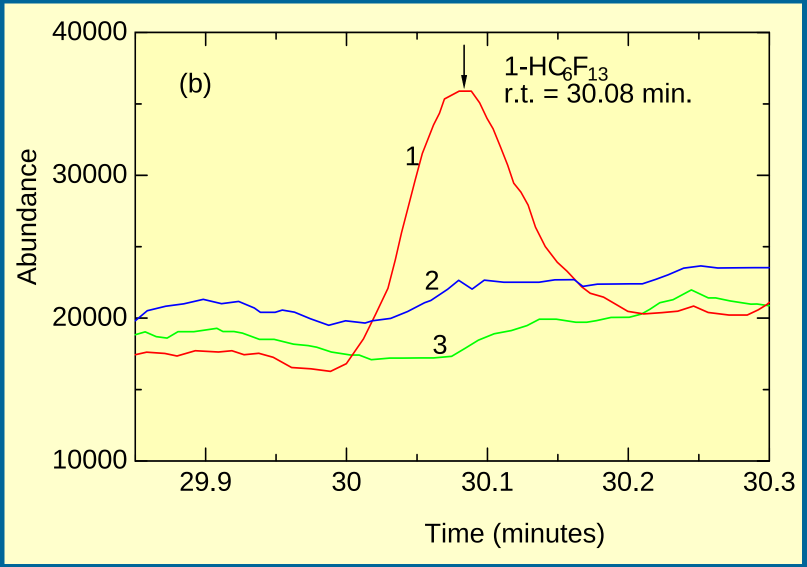
GC-TCD chromatograms for various perfluorocarbons: (1) C_3F_8; (2) n-C_6F_{14}; (3) iso-C_6F_{14}

• In contrast, the presence of the *H-containing* molecules (such as hexane, hydrofluoroalkanes, etc., curve 1) or of the *double bonds containing* ones (alkenes, hydrofluoroalkenes, perfluoroalkenes, etc.) could result in an increased radiation sensitivity of the cooling fluids.



GC-MSD chromatograms for the as received n-C_6F_{14} (1) and the purified (2) one;





Zoom on the GC-MSD chromatograms of n-C_6F_{14} impurified with:

(a) hexane: 1 – 300 ppm; 2 – 30 ppm; 3 – purified;

(b) 1-HC_6F_{13}: 1 - 300 ppm; 2 - 30 ppm; 3 – purified.

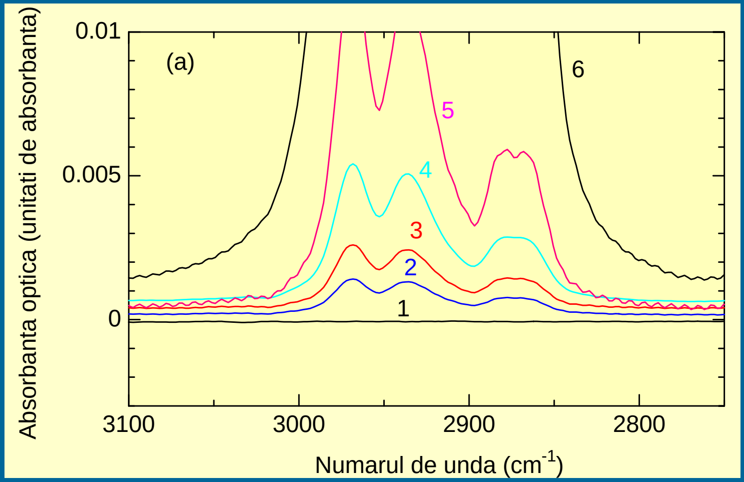
- The introduction of known and controlled impurities confirmed the assignment of the peaks. The detection limit found for these impurities was around 30 ppm owing the used analytical parameters.

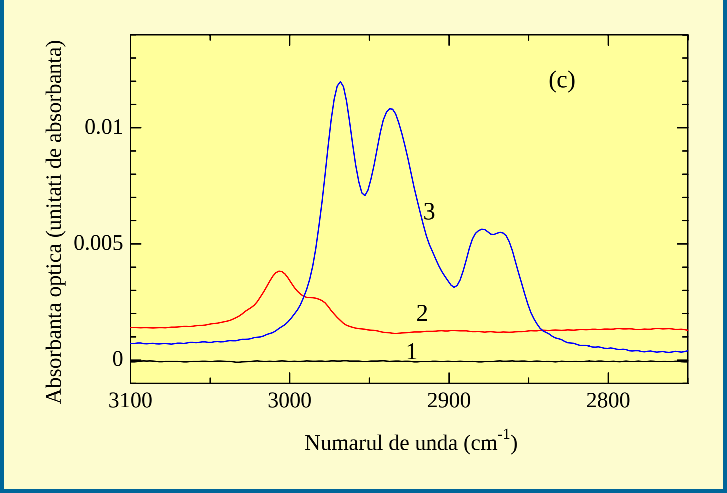
- The results of the purification tests confirmed a promising way to the removal of the undesired impurities.

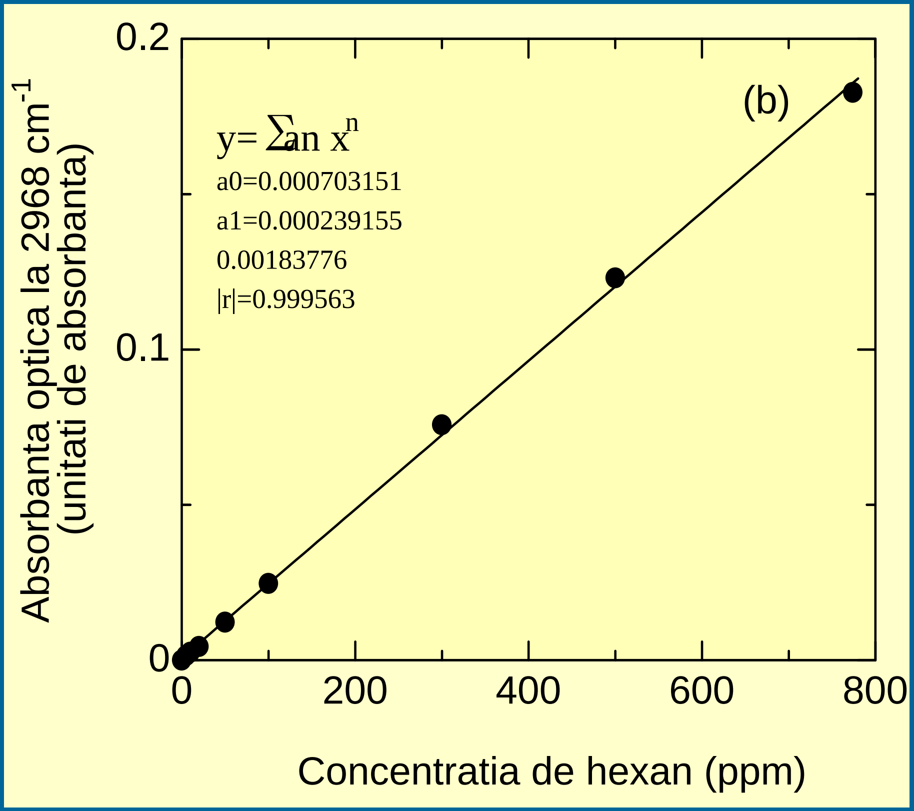
Examples of products observed in GC-MSD chromatograms of C_6F_{14} fluids

RT (minutes)	Assignement
4.42	H_2O + air
6.45	C_4F_{10}
9.43	C_5F_{12}
13.15	$CF_3CF(CF_3)CF_2CF_3$
13.50	cyclo-C_6F_{12}
15.40	C_6F_{14} (n, iso)
22.55	1-C_6F_{12}
23.50	Hexane
25.70 26.10	Homologous C_6F_{14} perfluorocarbons
30.08	H-C_6F_{13} (in PF 5060)

- Traces of high molecular weight oxygen containing fluorinated compounds (RT > 30 minutes) were In in PF 5060 fluid
- In PP1 were detected traces of higher molecular weight perfluorocarbons only



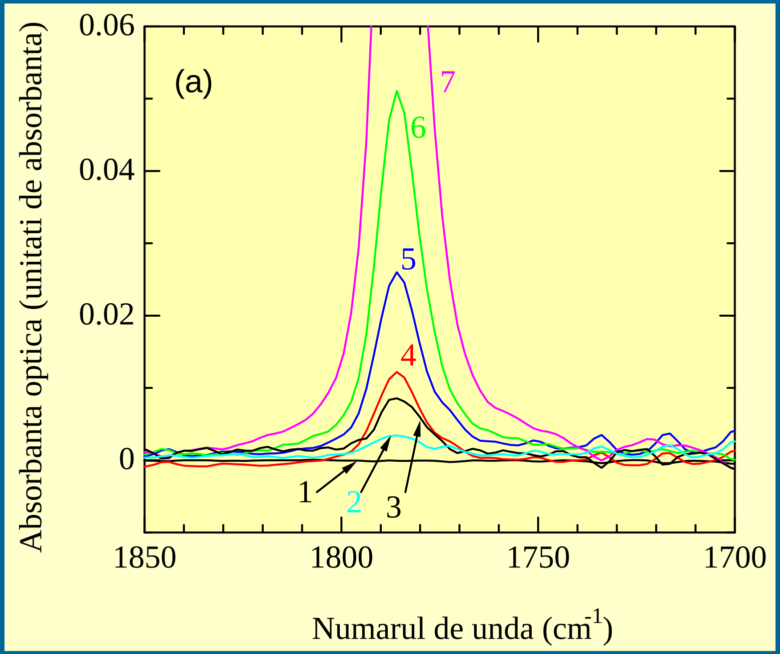


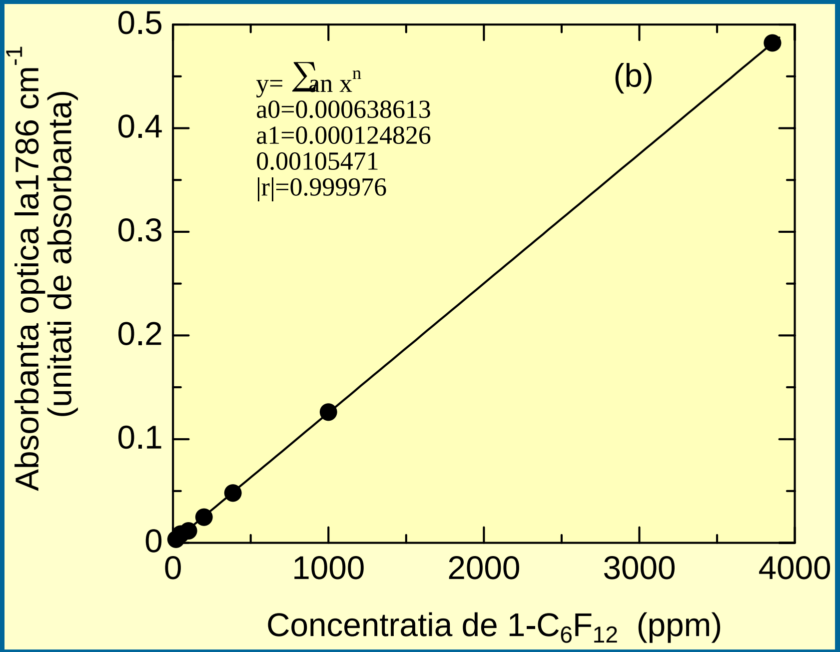


(a) FT-IR spectra in the region of 2900 cm^{-1} of n-C_6F_{14} containing different amounts of hexane:
1 - reference (purified n-C_6F_{14}; 2 - 5 ppm; 3 - 10 ppm; 4 - 20 ppm; 5 - 50 ppm; 6 - C_6F_{14} initial, as received

(b) The FT-IR calibration curve as a function of the hexane concentration and of the hexane like compounds

(c) Comparative spectra in the region of 3100 - 2800 cm^{-1} from controlled impurified C_6F_{14} : 1 - reference (pure C_6F_{14}); 2 - 1-HC_6F_{13} 300 ppm; 3 - hexane 50 ppm





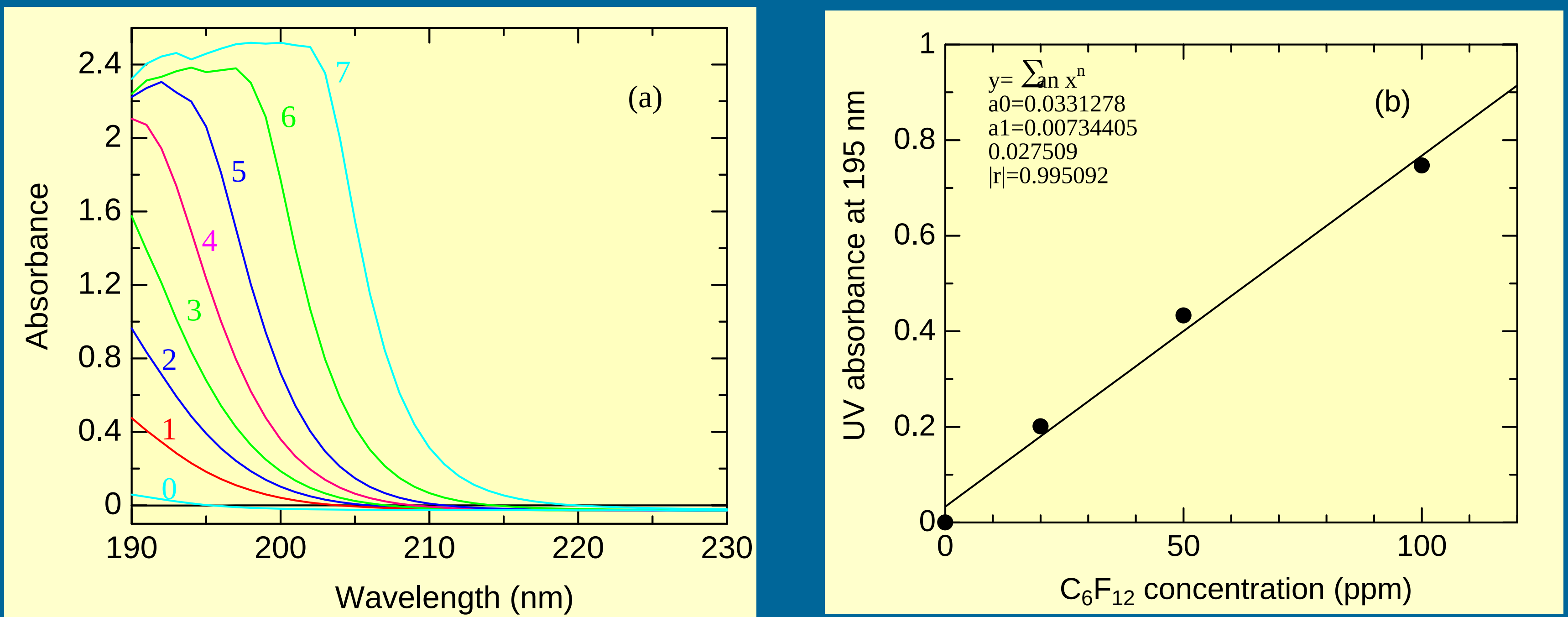
FT-IR spectra in region of 1780 cm^{-1} from C_6F_{14} samples impurified with C_6F_{12}:

1 - reference (pure C_6F_{12}); 2 - 20 ppm; 3 - 50 ppm; 4 - 100 ppm; 5 - 200 ppm;
6 - 386 ppm; 7 - 1000 ppm

(b) FT-IR calibration curve for determination of C_6F_{12}

•**UV-Vis** results are also consistent to the GC data, the optical absorption in the spectral range 190 - 220 nm being increased when perfluorohexene or 1-H perfluorohexane were added to pure $\mathbf{C_6F_{14}}$.

All as received samples exhibited a certain optical absorption in UV spectral range, which was strongly decreased following the purification treatment.



UV spectra in region of 190 – 240 nm from $C_6\mathbf{F_{14}}$ samples impurified with $\mathbf{C_6F_{12}}$:

1 - reference (pure $\mathbf{C_6F_{12}}$); 2 - 20 ppm; 3 - 50 ppm; 4 – 100 ppm; 5 - 200 ppm; 6 - 400 ppm; 7 - 1000 ppm.

(b) The UV calibration curve at 195 nm for the $\mathbf{C_6F_{12}}$ dosage.

Characterization of the initial fluids

Main results of the chemical characterization of the C_6F_{14} fluids: ✓ = test passed; test not passed

Parameter	Units	Required value		Fluid type			
		Lower limit	Upper limit	PP1	PF 5060 as received	DL	Purified PF 5060
C_6F_{14} purity by GLC (area %)*	%	98	-	99.259✓	98.964✓	99.023✓	99.052✓
Other PFC*	%	-	2	0.441✓	1.019✓	0.977✓	0.948✓
C_6F_{14} double bonded molecules	ppm weight	-	10	< detection limit ✓	detection limit ✓	< detection limit ✓	< detection limit ✓
H containing molecules (equiv hexane)[+]	ppm weight	-	10	< detection limit ✓	722	< detection limit ✓	< detection limit ✓
Free fluoride (equiv. HF)	ppm weight	-	1	0.05✓	0.06✓	0.03✓	0.02✓
Density	g/mL	1.660	1.700	1.721✓[++]	1.689 ✓	1.694✓	1.689✓
Boiling point	°C	51	59	56✓	56✓	56✓	56✓[x]

*From GC-MSD measurements
+The content in H-substitutes PFC was below the detection limit in all cases as shown both FT-IR, GC-MSD and GC-TCD measurements
++The CERN imposed density value refers to *n-C6F14*; the value found in literature for pure *perfluoro 2-methyl pentane (iso-C6F14*) is 1.723 [http://www.chemexper.com/]; that given by the supplier (F2) is 1.725 g/cm3 [Certificate of Analysis Batch No 0294/ Ref. No. P51917]. Thus, the measured density value corresponds to a pure fluid.

Characterization of the initial fluids

Main results of the chemical characterization of the C_3F_8 fluids: ✓ = test passed; ⬇ test not passed

Parameter	Unit	Lower limit	Upper limit	C_3F_8 (as analysed)
C_3F_8 organic purity*	% volume	99.96	-	99.964 ✓
Other perfluorocarbons*	ppm weight	-	400	360 (pefluorobutane) ✓
C_3F_8 double bounded molecules*	ppm weight	-	10	not detected ✓
H containing molecules*	ppm weight		10	not detected ✓
Free fluoride	ppm weight		0.1	0.08 ✓

*GC-MSD

Conclusions

- the Part I of the work was successfully accomplished;
- the chemistry laboratory analytical techniques and methods were sensitive to the parameters of interest and will be used for the future analyses of perfluorocarbon fluids;
- the following perfluorocarbon fluids supplied to CERN: PP1, PF 5060 DL and C3F8 were found compliant to the CERN quality requirements, while FC-72 and PF 5060 were not;
- the purification tests on less pure fluids were very promising; the potential suppliers and the acceptable quality of the fluids may be advantageously enlarged;

Thank you for yours attention!

I'am waiting for yours questions