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Development of a prototype for the recovery of R134a from the mixture of RPCs detectors

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CONTENTS

1. Abstract

The aim of this thesis work is to analyse in detail all the steps involved in the creation of a working prototype that can recover R134a gas from an azeotropic mixture. The various chapters are arranged in such a way as to follow the process and provide the information necessary for understanding the various operations.

The first chapter aims to give an explanation of why it is necessary to recover R134a, but especially where and why it is used. The discussion will take a top-down approach, starting with CERN and the LHC, and then moving on to the experiment that will house the prototype, CMS. Then the detectors using this type of mixture and more generally the gas system for muons detectors will be introduced. An overview such as this, and in particular going into detail about the gas system for muons detectors, is essential to understand the context, and since the R134a recovery system will be part of this complicated process, it is good to be fully aware of what can affect the system in question and vice versa.

Around 2018, a prototype had been developed to perform this task, but without success. Over time, following many unsuccessful tests, the problem was identified: R134a and the isobutane iC4H10 form an azeotropic mixture. Chapter 2 looks chronologically at the evolution of the prototype before arriving at the need to develop a new one. The configuration of this first prototype has been changed twice. This chapter will show the tests carried out on the last two configurations, carried out after the discovery of the azeotropic mixture. The study of these tests will make it possible to immediately identify the parameters that most influence the system and set as a goal for the subsequent prototype the optimisation of these to increase the efficiency of the system and the purity of the recovered gas.

Finally, the last two chapters will deal with the construction of the new prototype. They have been divided into two sections as they conceptually represent two phases that can be conducted in parallel. One deals with the steps relating to the design of the prototype, through the use of P&IDs and 3D drawings, and the construction of the prototype, while the other deals with the development of the logic and programming processes required for the prototype to function. From a chronological point of view, the steps to follow are the design of the prototype and with it the development of 2D

and 3D models, followed by the development of the process logic and its transformation into code readable by the future PLC. This is followed by the construction phase of the prototype and the analysis of its criticalities, as shown in the paragraph on leak tests, and finally everything related to the electrical and electronic components, which includes the construction of the rack that will house the PLC.

In conclusion, therefore, the aim of the thesis work is to follow the steps necessary for the realisation of a working prototype for the recovery of R134a gas. The studies and analyses carried out on the first version provide a better understanding of the fundamental parameters and solve the problems related to it. In addition, the need to manage a variable flow led to the design of the prototype.

2. High Energy Physics at CERN

Established in 1954, the European organization for nuclear research (in French Conseil européen pour la recherche nucléaire) know as CERN, it is located on the Swiss-French border, near to Geneva, but it is an European research organization, the most important one about the particle physics studies. The structure of the CERN is mainly composed by the LHC and other accelerator which provide the required energy to the particles in order to conduct the experiment.

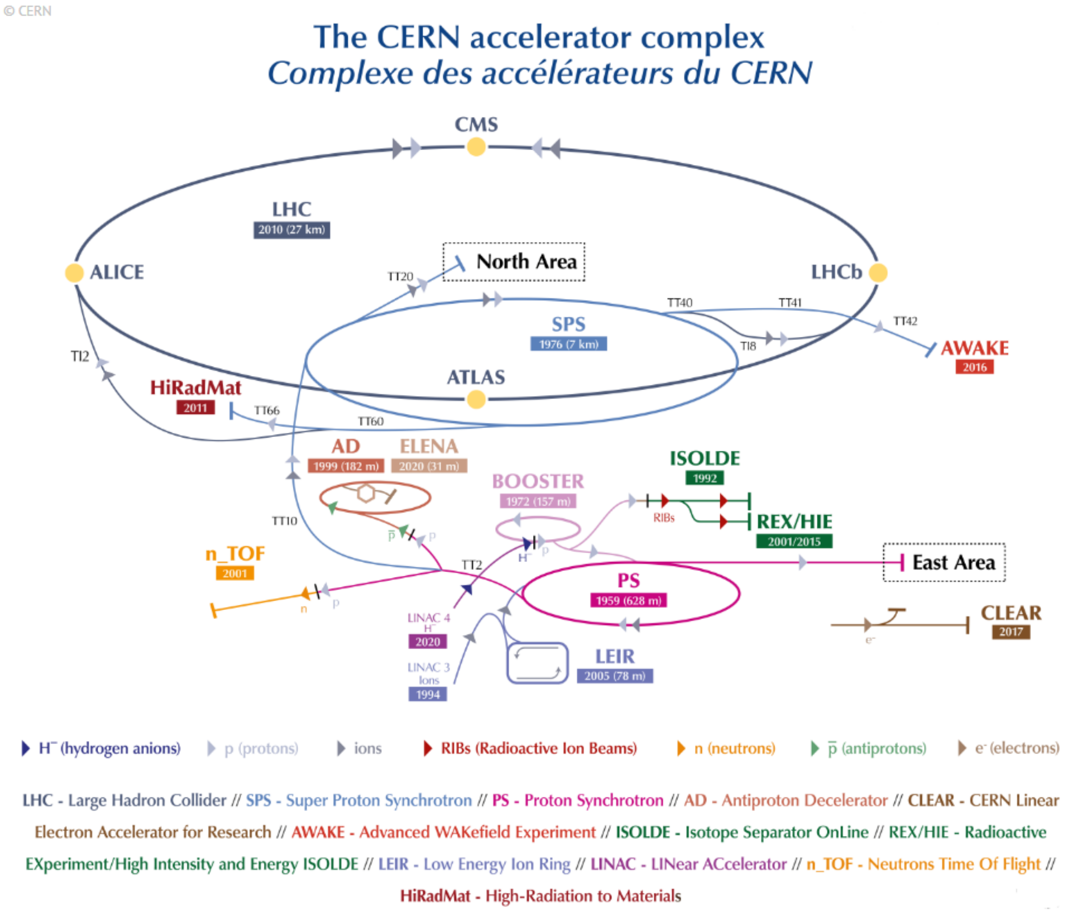

Figure 1: CERN accelerators complex layout [1]

Everything starts with LINAC – Linear Accelerator, that accelerates primary protons. These protons reach an energy level of 160 MeV useful to be prepared to enter in the Proton Synchrotron Booster (PSB) in which the negative Hydrogen loose all the electron and leaving only protons. The PSB accelerate the protons up to 2 GeV

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[1] E. Mobs, "The CERN accelerator complex - 2019," Cern Accel. complex - August 2018, Jul. 2019, Accessed: Jan. 29, 2021. [Online]. Available: https://cds.cern.ch/record/2684277.

required by the next accelerator called Proton Synchrotron (PS) in which the protons reach 26 GeV. Then they are injected in Super Proton Synchrotron (SPS) where they are accelerated up to 450 GeV. Finally, the protons are injected in the LHC in two different beam pipes where one beam circulates clockwise, and the other anti-clockwise. There they reach their maximum energy that is 6.5 TeV and circulate inside the LHC for many hours. At the end the two beams are brought into collision inside the 4 experiments: Atlas, Alice, LHCb and CMS where the total energy at the collision point is 13 TeV.

LHC can also accelerate different particles, like lead ions. These ions follow the same path of the protons, but they start from LINAC 3 that accelerates the ions from a source of vaporized lead, then they are sent to the Low Energy Ions Ring (LEIR) which provides the required energy to enter in PS and then the same way of the protons.

All of this energy given to the beam is used for studying particles, especially after collisions and it happens inside the LHC ring especially in four points. The main experiments that study these collisions are four: ATLAS, CMS, ALICE and LHCb.[2]

This work of thesis was done in CMS, and in order to understand better the purpose is necessary to give an overview of CMS, RPCs and gas system behind them.

2.1. CMS – Compact Muon Solenoid

CMS is one of the 4 big experiments of LHC at CERN, located 100 metres underground level near to Cessy, in France. It is 21 metres long, 15 metres wide and 15 metres high, a little bit smaller than ATLAS, and for this reason it is called "Compact".

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[2] E. Mobs, "The CERN accelerator complex - 2019," Cern Accel. complex - August 2018, Jul. 2019, Accessed: Jan. 29, 2021. [Online]. Available: https://cds.cern.ch/record/2684277.

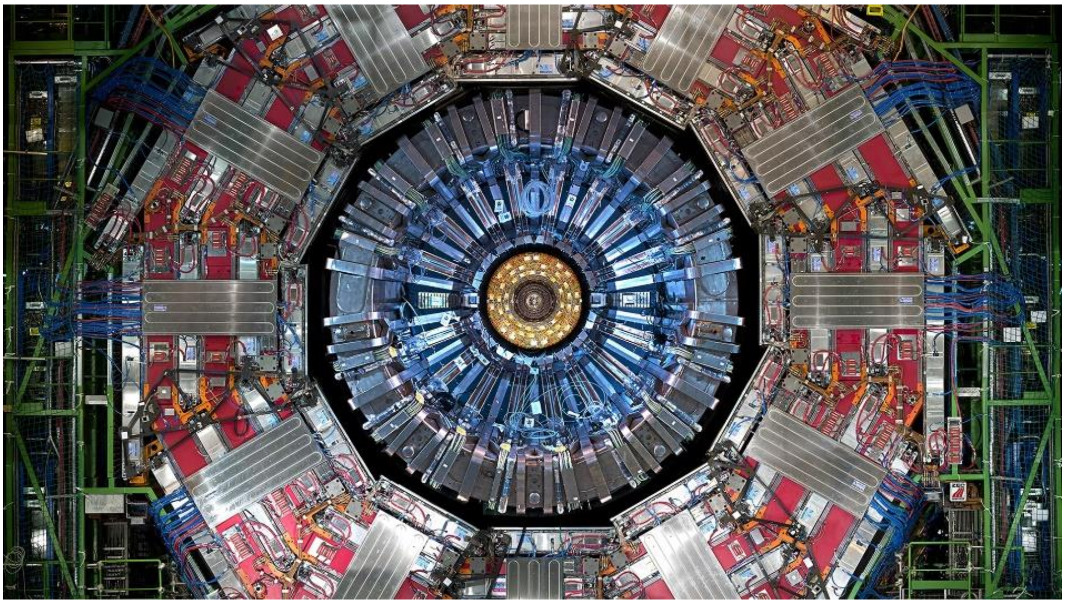

Figure 2: Picture of Compact Muon Solenoid [3]

It consists of a huge Solenoid with a cylindrical shape that generates a magnetic field of 4T, more than 100000 times the Earth's magnetic field. The aim of the solenoid, used in all large collider experiments is to allow the momentum measurements. The basic idea is that a magnetic field bends the path of a charged particle, and thanks to the silicon sensors it can be detected by electrical signal left along its path. The exact position of a particle is given by the interaction with the strip sensor or pixel, and in combination with several layer of them it is possible to reconstruct the path. Once it is done, it is possible to measure the radius of curvature of the track giving an estimation of the particle momentum by using:

$$p = R * 0.3B$$

Where "p" is the particle momentum in GeV/c, B is the magnetic strength in Tesla and R is the radius of curvature in metres.[4]

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[3] D. Barney, "CMS Slice," Feb. 2015. Accessed: Jan. 29, 2021. [Online]. Available: https://cds.cern.ch/record/2628641.

[4] D.Barney, "An Overview of the CMS experiment for CERN guides", Geneva, CERN,27 November 2003

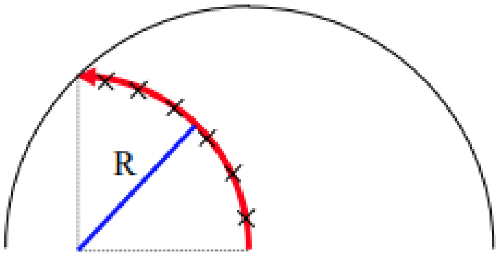

Figure 3: Schematic showing how the particle momentum is measured [5]

CMS, as ATLAS, has been specifically optimized for the detection and measurements of muons because they can easily identify and because they can only come from the decay of heavy particles which are the very interest of the collision research. The muon detectors are located in the outer area of CMS as shown in Figure 4.

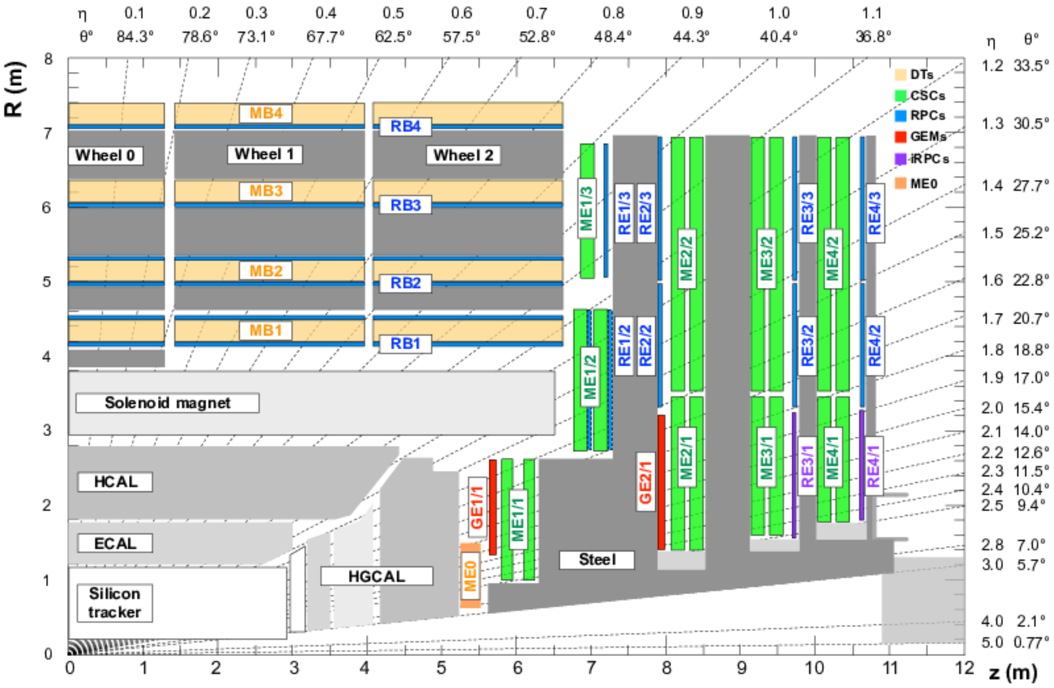

Figure 4: Graphic representation of the muon system in the CMS experiment [6]

In this schematic layout in Figure 4 is possible to see the four gaseous detectors used is CMS. In particular, Drift Tube (DT) chambers in the barrel and Cathode Strip

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[5] - D.Barney, "An Overview of the CMS experiment for CERN guides", Geneva, CERN,27 November 2003

[6] L. Guiducci, "CMS muon system towards LHC Run 2 and beyond," Nucl. Part. Phys. Proc., vol. 273–275, pp. 1014–1022, Apr. 2016, doi: 10.1016/j.nuclphysbps.2015.09.159

Chambers (CSC) in the endcaps, both integrated by a Resistive Plate Chambers (RPC) system and lastly the Gas Electron Multiplier (GEM). [7]

The position and the huge dimension of the detectors is justified by the fact that muons despite to other charged particles can go on their way for many metres. The next schematic image will show the cross section of CMS in which is represented the path of different charged particles. None of them exceed the super-conducting solenoid except muons.

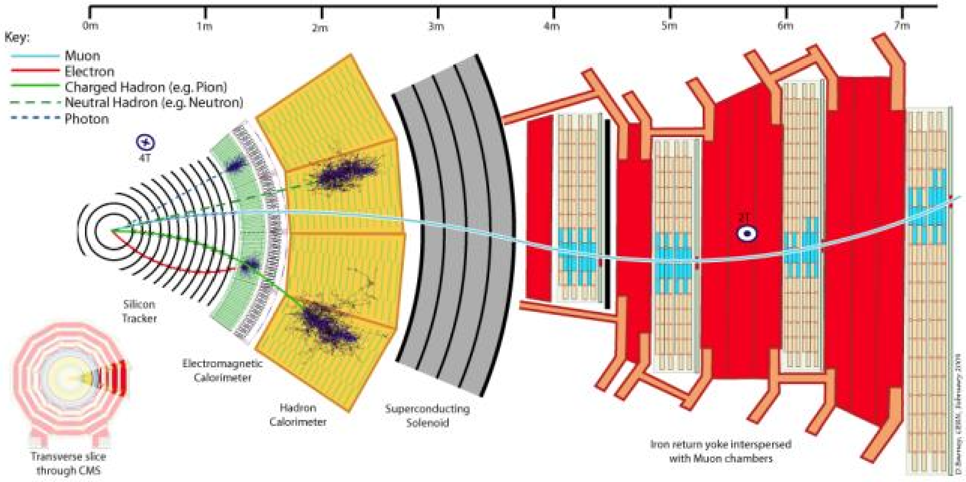

Figure 5: Cross section of the CMS experiment [8]

2.2. RPC – Resistive Plate Chamber

RPCs are one of the four gaseous detectors used for trigger and detect muons. Their application is high relevant because they can combine spatial resolution and time delay of just one billionth of second. They are made of two parallel charged plates separated by a thin gas volume. The principle of RPCs is that when a muon (or a charged particle) hit a gas molecule between the plates, is released an electron which in turn hit other

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[7] L. Guiducci, "CMS muon system towards LHC Run 2 and beyond," Nucl. Part. Phys. Proc., vol. 273–275, pp. 1014–1022, Apr. 2016, doi: 10.1016/j.nuclphysbps.2015.09.159

[8] An overview of the CMS experiment for CERN guides Preliminary version 0.1, Dave Barney, CMS Outreach Coordinator, 27 November 2003

gas molecules creating an avalanche of electrons. The electrode, made of high resistivity material, are transparent to the electrons, but they are picked up by external metallic strip after a small but precise delay time.[9]

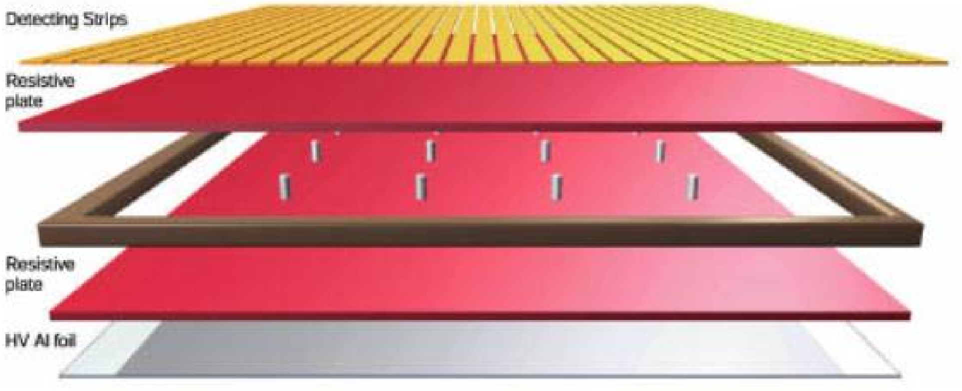

Figure 6: Schematic view of a RPC [10]

The gas mixture used by RPCs is mainly based on Freon in order to reach higher efficiency, but it is required also a small percentage of a gas that act as a quencher, like Isobutane and a gas that reduce the streamer probability like SF6.[11] The percentage are:

- 95,2 % of R134a (C2H2F4);
- 4,5 % of Isobutane (C4H10);
- 0,3 % of Sulfur hexafluoride (SF6).

To maintain a high quality and good performance of RPCs is strictly necessary to keep the percentages of the gas constant and to be sure of the purity of the mixture. This is the reason why it is requires a fresh gas mixture, but it also means that the exhaust mixture that come from the RPCs must be throw away. The continuous research to tackle climate change and greenhouse gas emissions conducted by the CERN has led to an efficient recirculation of 90 % of the mixture directed to the exhaust. For sure it

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[9] Resistive Plate Chamber – Cern https://cms.cern/detector/detecting-muons/resistive-plate-chambers
[10] Resistive Plate Chamber – Cern https://cms.cern/detector/detecting-muons/resistive-plate-chambers
[11] M. Abbrescia, V. Peskov, and P. Fonte, Resistive Gaseous Detectors. Wiley-VCH Verlag GmbH & Co. KGaA, 2018.

is a great result, but the 10%, mainly composed by R134a, must be separate from the gas mixture and stored.

2.3. Gas system for muons detectors

All gaseous detectors need a precisely designed gas system in order to provide an high quality and high stability of the gas mixture. Indeed, the fundamental parameter for the detectors operation and safety is the gas mixture which is provided by 30 dedicated gaseous system that can reach an extension of several hundreds of meters, observing severe requirements.

The gas system design follows a modular path in order to be adapted to each gaseous detectors requirements, but still having a common structure. Each module is implemented by a PLC (Programmable Logic Controller) that makes easy the monitoring and managing operation by authorised personnel.

The gas system infrastructure is organized in three section each one with its function. The buildings are located at three different level: The Surface room (SG), here are located all the units that need immediate access. The Service room (US), the first pre-distribution of gas into several channels and the Experimental Cavern (UX), which is the effective detailed distribution to each detector.

Furthermore, the gas system can be divided into unit blocks each with its own function and they are common to all systems. A brief explanation will be given for the main ones.

- *Gas Supply Monitoring System*: Each gas is provided by two independent supply sources, one in use and one in stand-by, that can compensate when there is a failure in the main one.
- *Mixer Module*: The gas mixture for each detector is prepared by this module starting from primary gases. Each mixer module has four input lines with their own mass-flow controller (MFCs) which can be controlled via software.

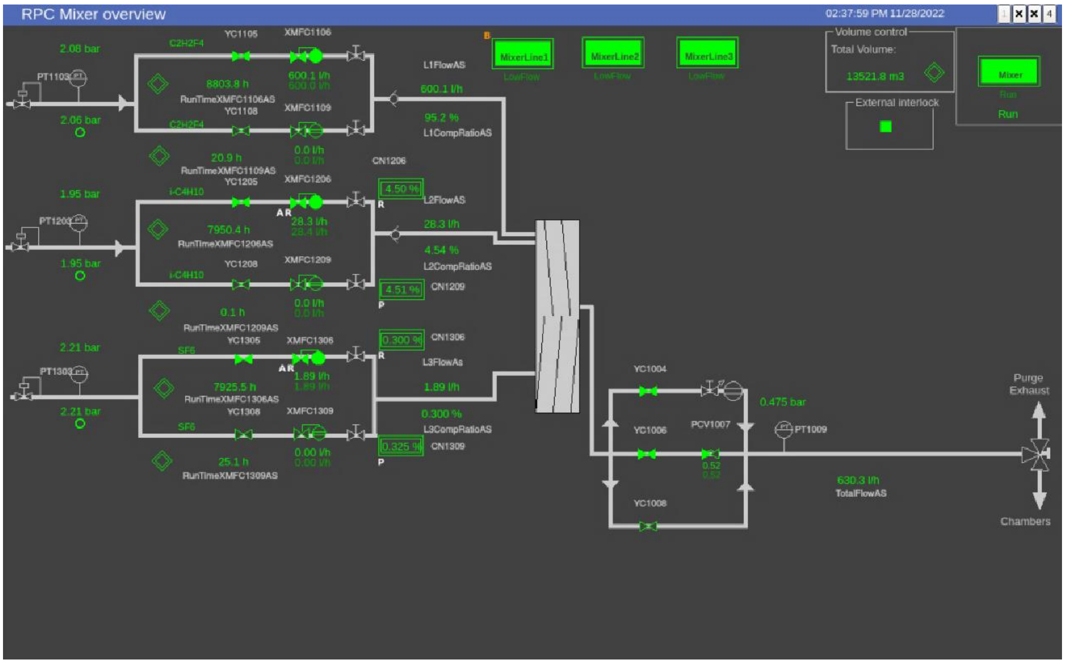


Figure 7: Scheme of RPC's mixer module

- *Gas Distribution*: It is located mainly in the US where pre-distribution modules are related to different detector sectors, and in UX where the lines are split in several smaller line in order to fit the requirements.
- *Pump Module*: After the detectors the gas has to be collected and send back to the circulation module at the surface. Then the compressed gas could be re-circulate or wasted.

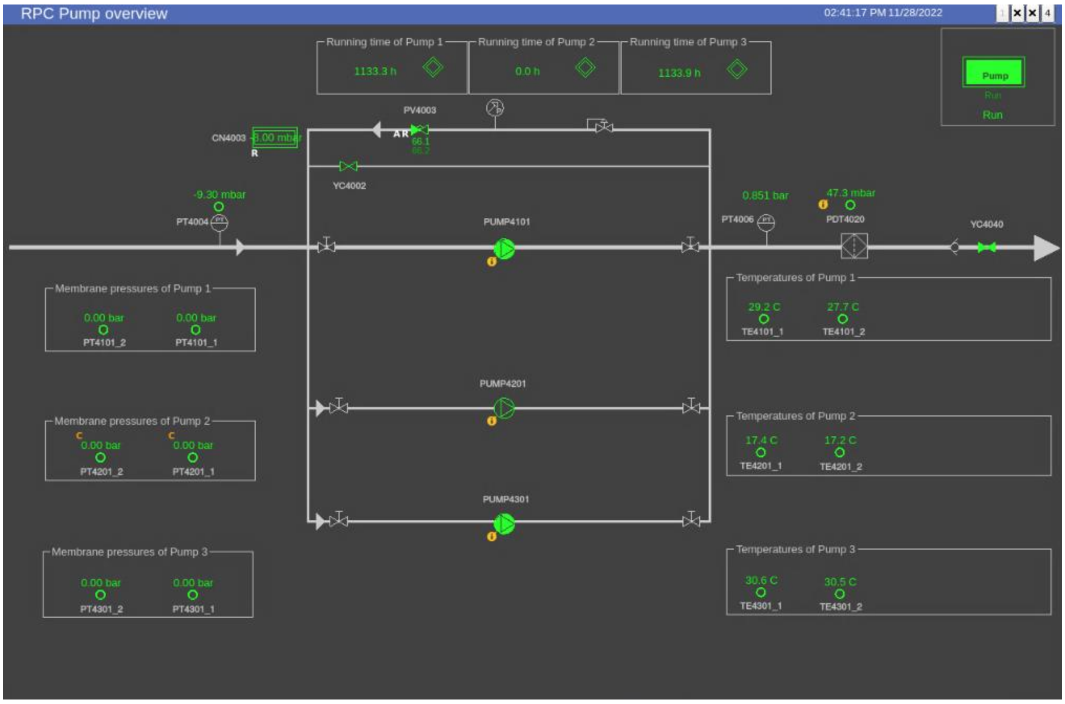
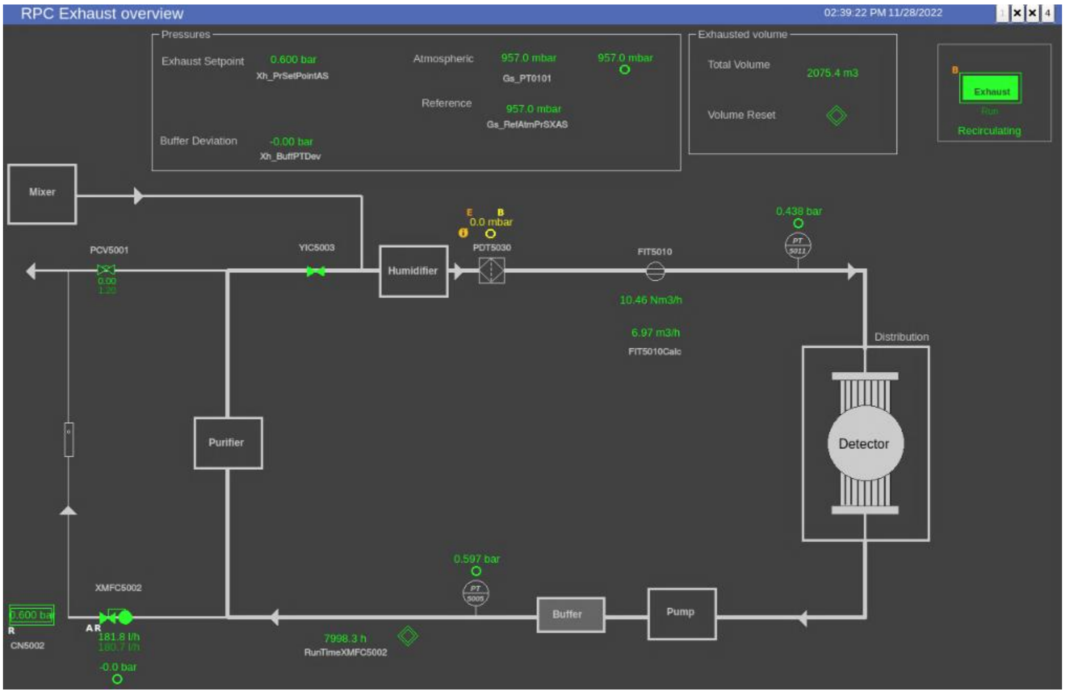


Figure 8: Scheme of RPC's Pump module

- *Exhaust module:* The main aim of this module is to collect the gas which can not be used anymore and throw them away into the atmosphere, controlling the recirculation function. In the scheme shown in Figure 9 there are in the lower part of the loop the two main components, a mass-flow controller, and a pressure sensor. These two elements are connected each other in order to maintain the pressure inside the loop constant.



Exhaust Setpoint 0.600 bar Xh_PrSetPointAS
Atmospheric 957.0 mbar Gs_PT0101 957.0 mbar
Reference 957.0 mbar Gs_RefAtmPrSXAS
Buffer Deviation -0.00 bar Xh_BuffPTDev
Total Volume 2075.4 m3
Volume Reset

Figure 9: Scheme of RPC's exhaust module

- *Gas Analysis Module*: The high quality of the gas is the main requirement for the detectors, for this reason a continuous monitoring system is installed. The main purpose is to detect impurities or, as in CMS and LHCb, GCs modules which can monitor complex impurities.
- *Gas Recuperation Module*: The gasses used are often expensive and greenhouse gasses, for this reason a recuperation system that separates and stores it can help the environment and contain the operational costs. Typical recuperated gases are Xe, C_4F_{10}, CF_4,C_5H_{12} and is now developing a new recuperation system with the aim of recuperate R134a from exhaust gas mixture of RPCs.

The recuperation module is not the only way to reduce costs and pollution, but it can also be done recirculating a part of the gas mixture that come out from the gaseous detectors. In fact, the gas mixture can be collected, after the detectors and re-inject into the supply lines. This operation could favour the accumulation of impurities such as N_2 O_2 H_2O. It necessary a purification system which significantly reduce the amount of oxygen, with metallic catalyst and water with molecular sieves. Not all the gas mixture can be recirculated, so the part that is sent to the exhaust is replaced by fresh gas from mixer module.

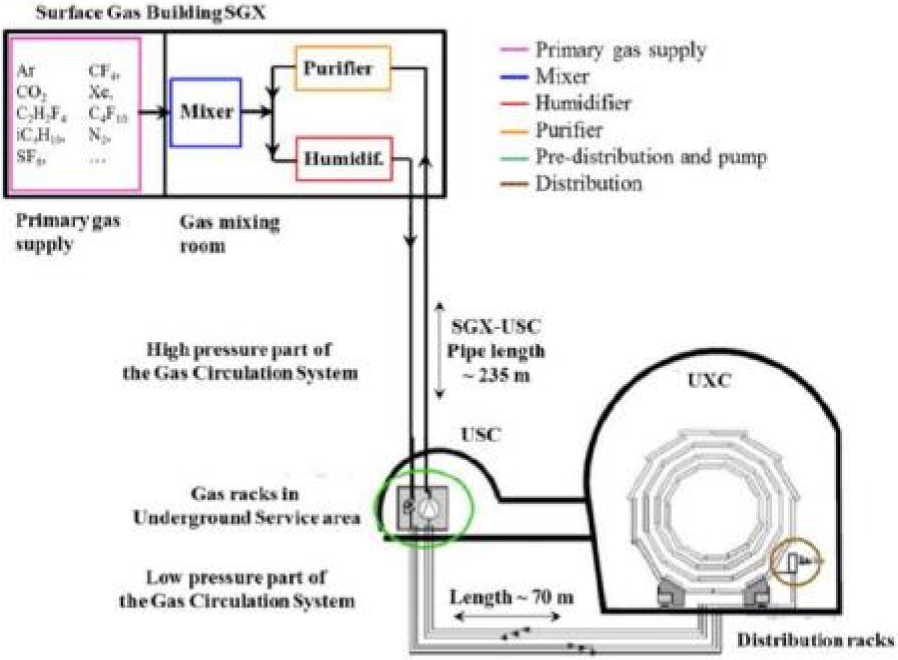


Figure 10:Schematic representation of gas system for LHC experiment [12]

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[12] R. Guida, M. Capeans, F. Hahn, S, Haider, B. Mandelli, The gas systems for the LHC experiments, 2013, CERN, Geneva, Switzerland.

3. R134a Recuperation system Prototype “I”

The introduction made before is useful to give a general overview and understating better the purpose of this work of thesis.

RPC’s gas mixture used is made of 95,2% of R134a, 4,5% of i-C4H10 and 0,3% of SF6 and since R134a and SF6 have a Global Worming Potential (GWP) of 1430 and 23900 respectively, they are classified as greenhouse gases. CERN has implemented several strategies in order to reduce the emissions of these gases into the atmosphere, like the recirculation system described before and the recuperation system which is the object of this work of thesis.

Concerning the RPC’s gas mixture, it is necessary to recuperate and re-use the R134a, since it is the main component of the mixture, and it has an high value of GWP. From the outset, the idea was to position the recovery system downstream of the purifier so that a mixture of R134a Isobutane SF6 and air would enter our system. Figure 10 shows the screenshot of the monitoring software in which the entire gas system is visible, with the different modules mentioned above. Also highlighted is the connection point of the system with the R134a recovery system, positioned after the two purification modules.

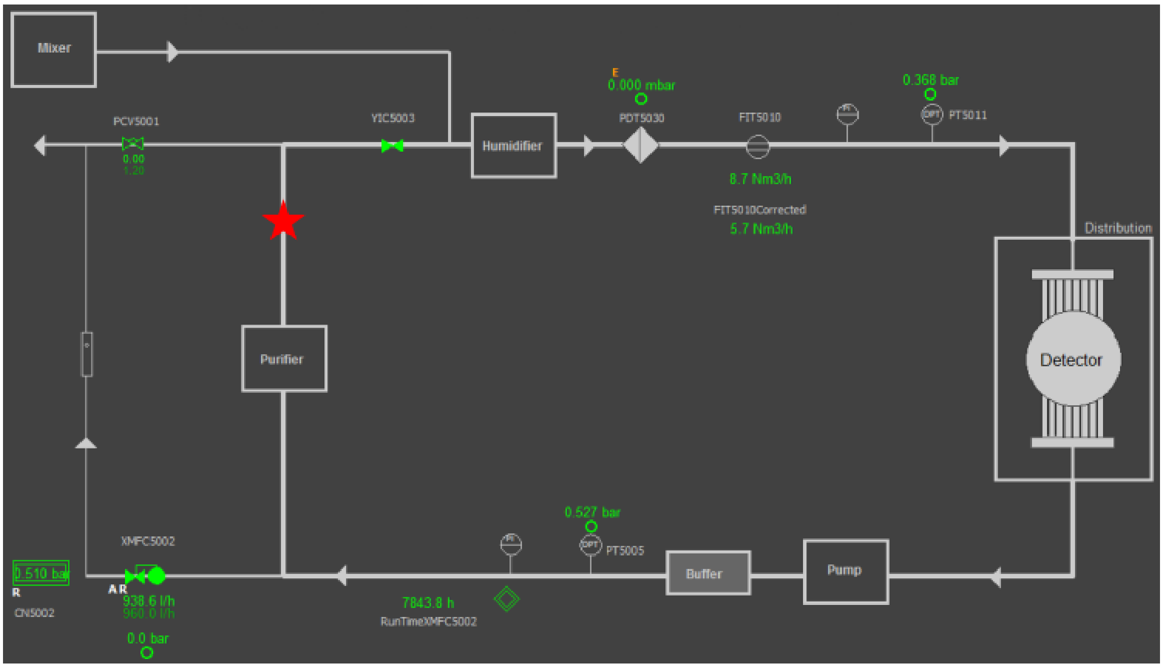

Figure 11: Scheme of RPC exhaust, where the prototype is placed.

Initially, the idea behind recovery was to extract the freon from the mixture by means of a simple distillation process, which involves, in the case of two gases for example, bringing the mixture to a sufficiently low temperature to the point where a perfectly distinct liquid and gas phase of the two gases is obtained. Based on this idea, the first prototype was built, which operated in two distinct phases. The first would reach the liquefaction temperature of the isobutane, allowing pure isobutane in the liquid phase, and thus separate R134a air and Sf6 in the gas phase. Then cool the remaining part of the mixture to a temperature where the Freon liquefies, allowing it to be stored.

The diagram in Figure 12 thus represents the first prototype realised. You can see the cooling systems reaching temperatures of -37°C and the two volumes in which the distillation process takes place. In the first, the liquefaction of isobutane takes place, and in the second, that of freon.

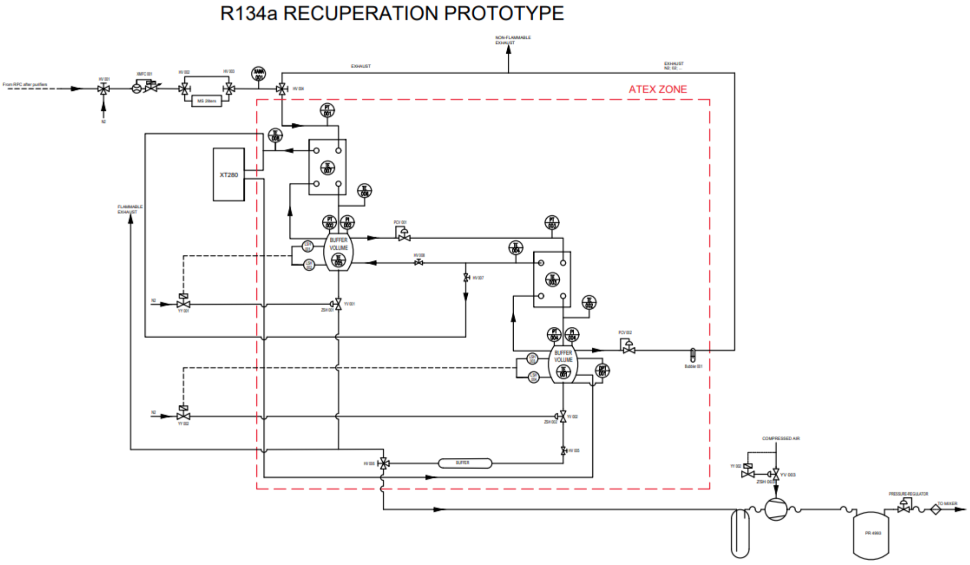

Figure 12: First schematic representation of the recuperation system

The first test conducted showed an high percentage of isobutan which is not in line with the expected results. The reason behind is that during the distillation process not all the isobutan is separate from the gas mixture. This observation opend the research in the field of the azeotropic mixture.

3.1 Azeotropic Mixture

The molecular interactions are the reason why mixtures form liquid phase, but sometimes these forces are too strong to separate the components. In this case the liquid phase and the vapour phase at equilibrium shown the same composition at given pressure and temperature range, and this makes the mixture impossible to separate using common techniques. These specific types of mixture are called azeotropes. The name comes from the Greek word "azeotropos" thant means "nonboiling by any means" (a – non, zeo – boil, tropos – way). The main feature is that the mixture boils at a different temperature of the boiling point of the pure components. It can be lower or higher according to the different type of azeotropic mixture.

A simple liquid mixture is easily separated since the vapour phase is enriched by the more volatile components and depleted by the less volatile components. Repeating this process and segregating the vapour phase it is possible to reach the desired degree of separation. This is not valid for the azeotropic mixtures since it is impossible to enrich the vapour phase at the azeotropic point. They need more sophisticated techniques to separate the two components which can be divided in three different class:

- Enhanced distillation;
- Membrane process;
- Process intensification.

The first class modify the distillation process enhancing conditions and configurations. The second class use membrane separation methods such as pervaporation processes, but it is still limitated due to the fact that it is not yet proven its efficiency in large scale applications. The third class take into account the research in novel apparatus and techniques, optimizing the economical, environmental and enegetical aspects.[13]

A brief summary of the different technique is shown in the Figure 13.

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[13] E.-K. Hilmen, "Separation of Azeotropic Mixtures: Tools for Analysis and Studies on Batch Distillation Operation," 2000.

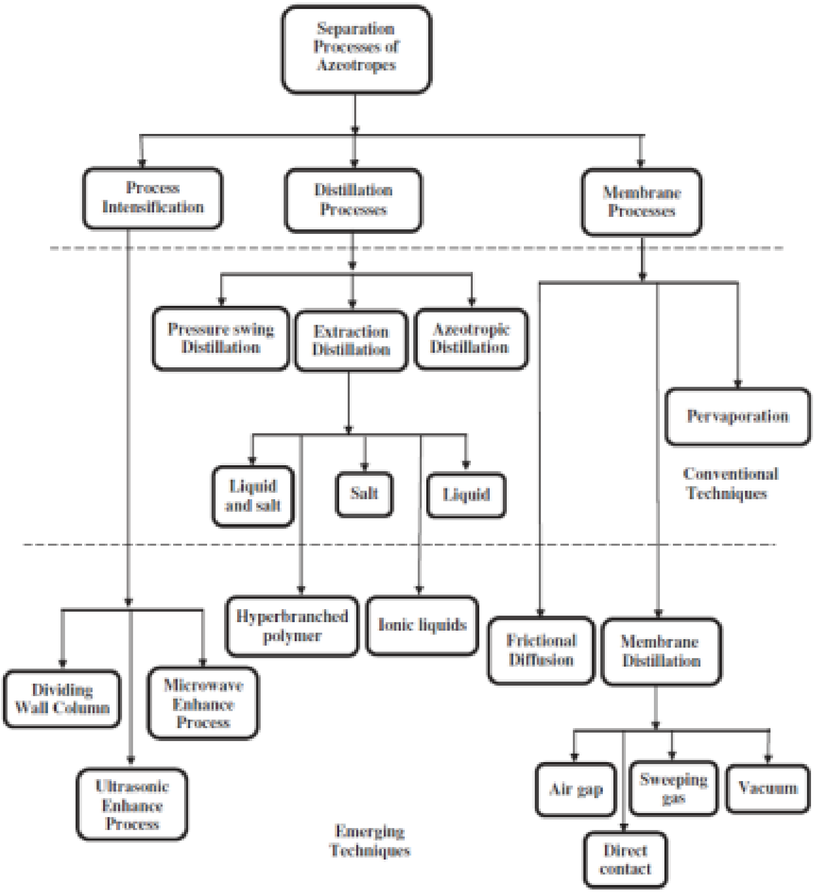

Figure 13: Schematic representation of the different separation process techniques [14]

The azeotropic mixture formed by R134a and C4H10 is a minimum boiling azeotrope, which means that the boiling point of the mixture is lower thant the boiling point of the pure components.

Component	**Concentration**	**Boiling point at atm P**
iC_4H_{10}	4.5%	-12 °C
R134a	95.2%	-26.3 °C

Table 1: Boiling temperature of R134a and Isobutane

Raoult's law links pressure of the fluids with their temperature and concentrations of an ideal mixture on the liquid-vapor equilibrium. The azeotropic point consists in a deviation of this law when the intramolecular forces between molecules of the same

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[14] F. Cambiè "R134a separation and recuperation from the gaseous mixture used in the Resistive Plate Chamber detectors at the CMS Experiment", Geneve, CERN, 2021

species is higher than the forces between different molecules. The specific case of R134a/iC4H10 is shown in the following picture, and show the minimum azeotropic point at the composition 65/35 molar fraction at -32.5 °C, setting the process at atmospheric pressure.

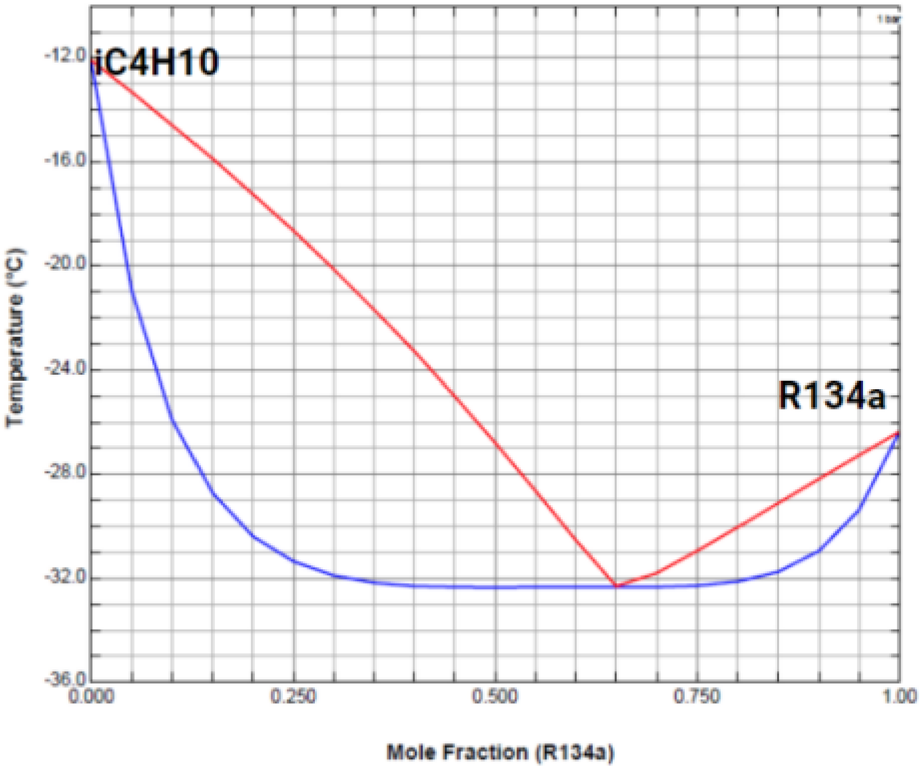

Figure 14: Azeotropic mixture between R134a and Isobutane [15]

The specific phase diagram of the two component, in Figure 14, was obtained with the software REFPROP[16] which allows to compute the thermodynamic properties of many gases and their mixtures.

In our case the RPC's gas mixture has a composition of 95/5 R134a/iC4H10. The process will happen in the right lobe of the diagram, and the distillation process can be treated as a "ideal" distillation between the R134a as less volatile component and azeotrope mixture as more volatile component ($T_{boil}^{R134a} > T_{boil}^{AzeoMix}$). This is due to

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[15] F. Cambiè "R134a separation and recuperation from the gaseous mixture used in the Resistive Plate Chamber detectors at the CMS Experiment", Geneve, CERN, 2021

[16] NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP): Version 10. URL: https://www.nist.gov/srd/refprop.

the fact that during the distillation process of a minimum azeotrope, the distillate tends towards azeotropic composition, while the component initially present in excess of the azeotropic composition remains as a residue of distillation.[17]

Starting from the conditions described above the distillation needs to follow a quasi-static process where the temperature is increased slow and with infinitesimal steps. The starting point is the operating condition, R134a/iC4H10 95/5, then the final step is 100% of the concentration of R134a. In this process there is not a separation of the azeotropic mixture, but as introduced before, the azeotropic mixture is separated from the R134a that is in excess in the mixture. At the end there will be some losses of pure R134a, so an efficiency of the process is necessary in order to improve and optimise the operating conditions.

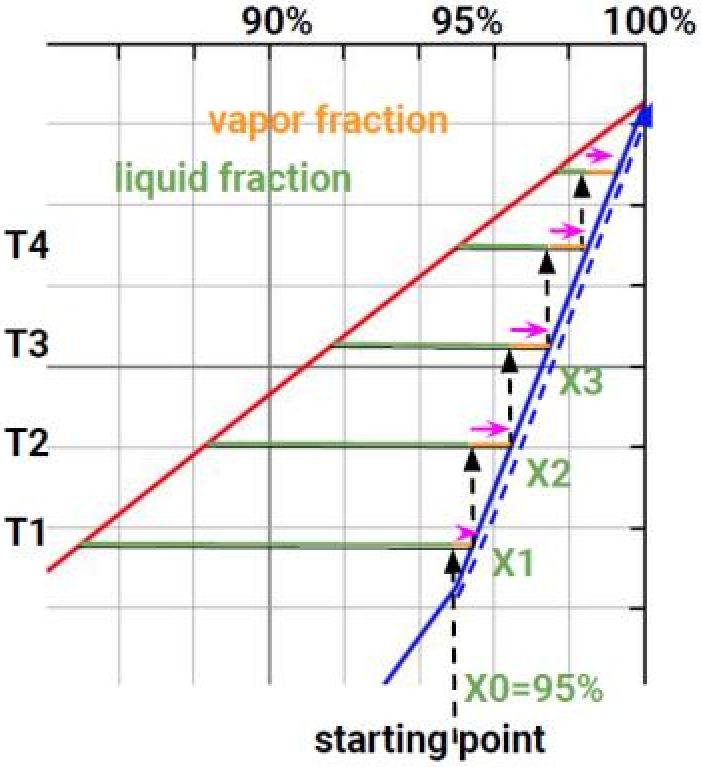

Figure 15: Schematic representation of the step for R134a enrichment. [18]

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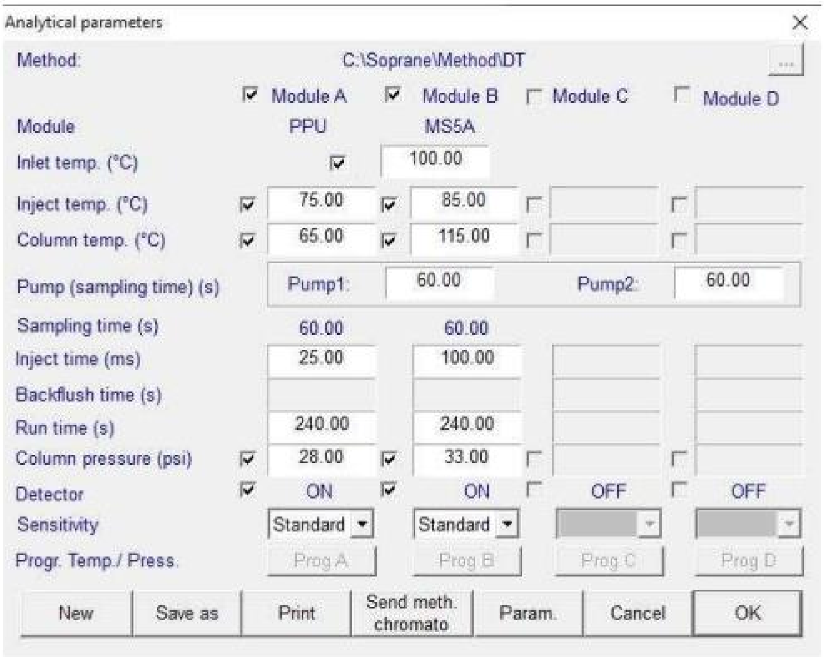
[17] Soluzioni non ideali: deviazioni dalla legge di Raoult e azeotropi https://www.appuntimania.com/scientifiche/chimica/soluzioni-non-ideali-deviazion63.php

[18] F. Cambiè "R134a separation and recuperation from the gaseous mixture used in the Resistive Plate Chamber detectors at the CMS Experiment", Geneve, CERN, 2021

In the Figure 15 it is possible to see the process explained above. Starting from the 95% of the concentration the temperature is increased, then the vapor fraction in removed and it brings the mixture to a new concentration. The steps are repeted untill the mixture has reached the 100%.

3.4 Gas Chromatography

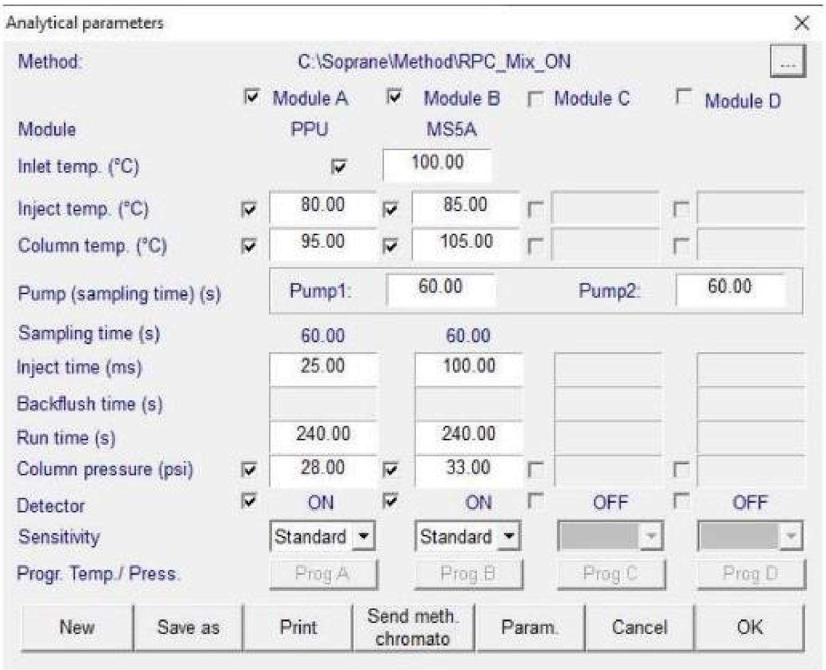
Analysing gas mixtures makes it possible to monitor the state of the gas systems of the LHC experiments. In particular, the gas detectors, which use different types of mixtures, are analysed on a bi-weekly basis using special instruments, the Gas Chromatographs. The prototype of R134a recovery requires the same control, especially during experimentation to observe any traces of other unwanted components. For this purpose, a microGC was adopted, a compact GC created by integrating micro-components. It consists of a microinjector, one or more analytical columns and dedicated Thermal Conductivity Detectors (TCD). This has the advantage of performing analyses within a few minutes thanks to shorter analytical columns than standard GCs. The CMS' gas systems status is monitored bi-weekly for DT, CSC and RPC gas mixtures. Each mixture requires a dedicated 'method' to be analysed, where temperature and pressure parameters are set to ensure the best separation of components.


Analytical parameters

Method: C:\Soprane\Method\DT

	☑ Module A	☑ Module B	☐ Module C	☐ Module D
Module	PPU	MS5A		
Inlet temp. (°C)	☑	100.00		
Inject temp. (°C)	☑ 75.00	☑ 85.00	☐	☐
Column temp. (°C)	☑ 65.00	☑ 115.00	☐	☐
Pump (sampling time) (s)	Pump1: 60.00		Pump2: 60.00	
Sampling time (s)	60.00	60.00		
Inject time (ms)	25.00	100.00		
Backflush time (s)				
Run time (s)	240.00	240.00		
Column pressure (psi)	☑ 28.00	☑ 33.00	☐	☐
Detector	☑ ON	☑ ON	☐ OFF	☐ OFF
Sensitivity	Standard	Standard		
Progr. Temp./ Press.	Prog A	Prog B	Prog C	Prog D

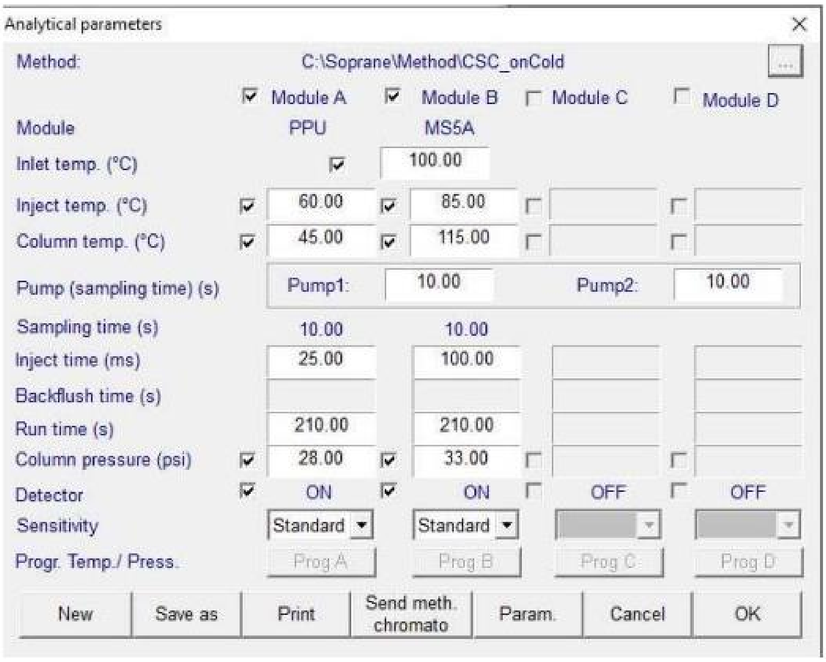
Figure 16: µGC method for DT


Analytical parameters

Method: C:\Soprane\Method\RPC_Mix_ON

	☑ Module A	☑ Module B	☐ Module C	☐ Module D
Module	PPU	MS5A		
Inlet temp. (°C)	☑	100.00		
Inject temp. (°C)	☑ 80.00	☑ 85.00	☐	☐
Column temp. (°C)	☑ 95.00	☑ 105.00	☐	☐
Pump (sampling time) (s)	Pump1: 60.00		Pump2: 60.00	
Sampling time (s)	60.00	60.00		
Inject time (ms)	25.00	100.00		
Backflush time (s)				
Run time (s)	240.00	240.00		
Column pressure (psi)	☑ 28.00	☑ 33.00	☐	☐
Detector	☑ ON	☑ ON	☐ OFF	☐ OFF
Sensitivity	Standard	Standard		
Progr. Temp./ Press.	Prog A	Prog B	Prog C	Prog D

Figure 17: µGC method for RPC



Method: C:\Soprane\Method\CSC_onCold

	☑ Module A	☑ Module B	☐ Module C	☐ Module D
Module	PPU	MS5A		
Inlet temp. (°C)	☑ 100.00			
Inject temp. (°C)	☑ 60.00	☑ 85.00	☐	☐
Column temp. (°C)	☑ 45.00	☑ 115.00	☐	☐
Pump (sampling time) (s)	Pump1: 10.00		Pump2: 10.00	
Sampling time (s)	10.00	10.00		
Inject time (ms)	25.00	100.00		
Backflush time (s)				
Run time (s)	210.00	210.00		
Column pressure (psi)	☑ 28.00	☑ 33.00	☐	☐
Detector	☑ ON	☑ ON	☐ OFF	☐ OFF
Sensitivity	Standard	Standard		
Progr. Temp./ Press.	Prog A	Prog B	Prog C	Prog D

Figure 18: µGC method for CSC

The importance of having a dedicated method for a proper separation of the components will be better addressed in the following paragraphs, particularly with regard to the RPC gas mixture.[19]

WORKING PRINCIPLES OF µGC

The gas mixture to be analysed is injected through the micro-injector into the GC, together with a carrier gas which can be Ar, N2, H2, He. The choice of carrier gas is made on the basis of the specific properties of the chosen column type and the mixture to be analysed. The temperature, set in the 'method', is controlled by an oven. It is a fundamental parameter as it is responsible for the separation of the mixture into its constituent gases. Generally, the time for the separation to take place is about 180s. The mixture separates into its constituent gases due to the specific chemical species covering the inner surface of the column that have different interaction forces with the mixture components.

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[19] M.C. Arena “Optimization of cf4 recuperation from the gas mixture used in the csc gas system at the compact muon solenoid (cms) experiment at CERN”, Geneve, CERN, 2021

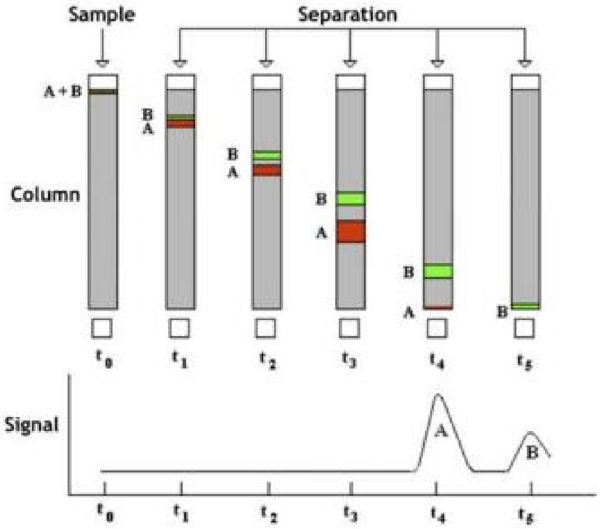

Figure 19: Schematic representation of the separation process inside a µGc column.

There are two types of columns, the capillary and the packed ones. The GC at CMS is a µGC Agilent R3000 equipped only with capillary columns of two different types:

- PPlotU: Porous Layer Open Tubular column. Stationary phase is Divinylbenzene/Ethylen glycoldimethacrylate. It separates C1 to C4 hydrocarbons, CO2, CH4, H2O, H2S, SO2, and N2O;
- MolSieve: 5Å zeolite molecular sieve. It separates permanent and noble gases: Ne, H2, O2, Ar, N2, CH4, CO;

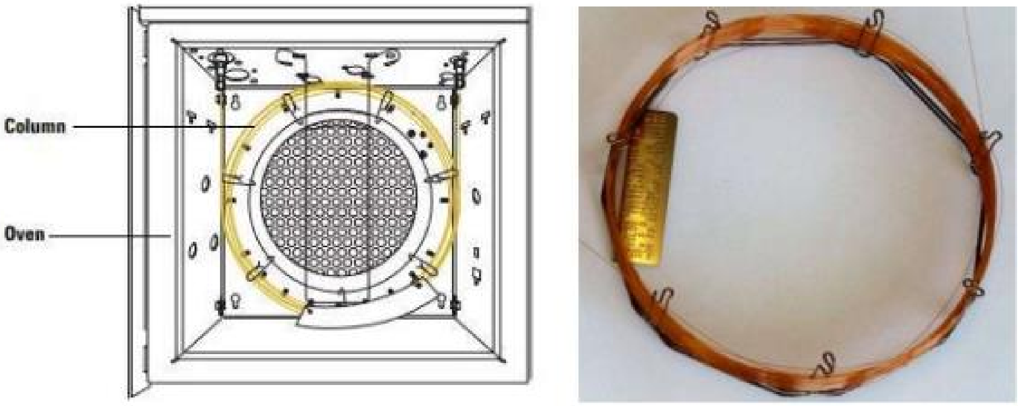

Figure 20: Schematic representation and image of a typical µGc column and oven.

Figure 20 shows a schematic of a typical micro GC, illustrating how the column is heated inside the oven. It is possible to distinguish the two most important variables for proper analysis and separation, namely oven temperature and column length. To these variables, the choice of carrier gas must be added.

The detection of the different components is carried out by a thermal conductivity detector whose signal is proportional to the amount of gas leaving the column. The result of the analysis is a Chromatogram, a time course of the different concentrations of the different components in the mixture. The parameters are retention time and peak size. The former is useful for identifying the component, the same components have the same retention times, the latter, considering peak height and area, is a measure of the concentration of the component. TCD consists of electrically heated filaments in a cell at a constant temperature. Depending on the thermal conductivity of the components passing through the cell, the filaments change their resistance, which is measured with a Wheatstone bridge circuit. Two paths are available, one occupied by the reference gas and the other occupied by the analytical column gas. The signal is calibrated to zero when the gas occupying the analytical column is a pure carrier gas.

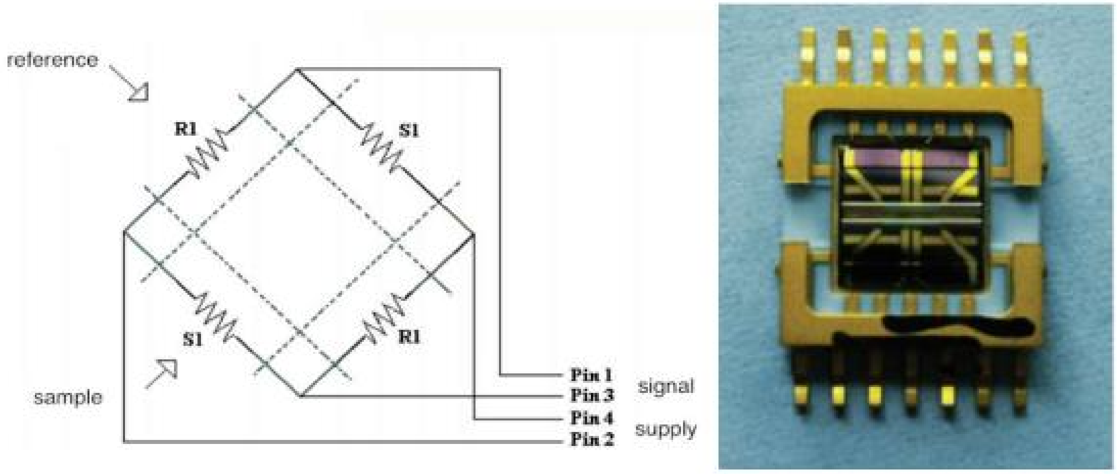

Figure 21: Schematic representation of Wheatstone bridge (left) and universal detector based on Micro ElectroMechanical System (MEMS) 10 times more sensitive than conventional Thermal Conductivity Detectors (right).

The measurement of the signal takes place thanks to the fact that the analytical flow, containing different polyatomic molecules each with different thermal capacities, causes the temperature of the filament to vary. This phenomenon unbalances the bridge and thanks to electronic instruments the signal is amplified to obtain the chromatogram. The reference gas (carrier gas) passes through the filaments R1 (Figure 21). The analytical flow from the column passes through the S1 filaments. Pins 1 and 3 provide the signal measurement. Pins 2 and 4 are for the power supply of the bridge.The concentration of the analyte is therefore proportional to the voltage signal produced. Starting from a few ppm up to 100%, the dynamic and linear response for 0-20% concentrations, but flattens immediately after them. For this reason a calibration is required to calculate the concentration value from the raw signal.

To avoid inaccuracies in the concentration calculation, a calibration is necessary. In the graph shown in Figure 22 you can see the trend of the conversion factor obtained by measuring the area of the CF4 peaks in reference mixtures with increasing CF4 content (5%-100%). It can be seen that the trend is almost linear for lower concentration values, and then its slope decreases. It is therefore necessary to calibrate with a reference mixture that is as close as possible to that of the sample.

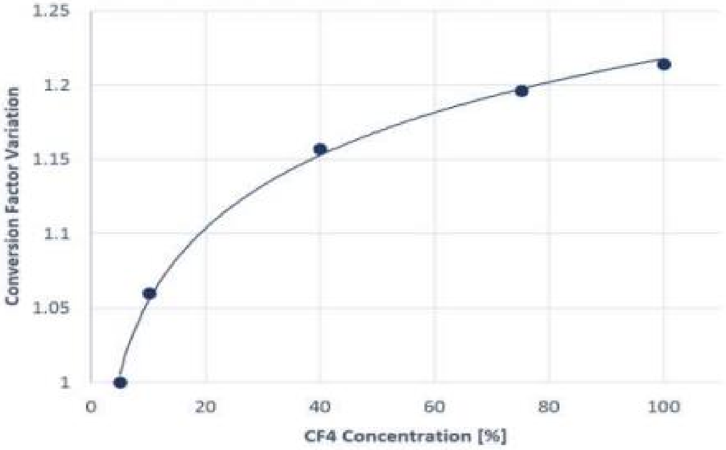

Figure 22: Example of CF4 calibration curve, obtained analysing mixture with known concentration of CF4 [20]

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[20] M.C. Arena "Optimization of cf4 recuperation from the gas mixture used in the csc gas system at the compact muon solenoid (cms) experiment at CERN", Geneve, CERN, 2021

3.2. 1^{st} modification of the Prototype “I”

The discovery of an azeotropic mixture represented a big challenge for the first designed system which was projected to do a “simple” distillation process. With the buffers in this configuration, it is impossible to operate a distillation process like the one described above. Which is why a change was necessary in the design of the system. The following schematic representation show the modifications done on the system.

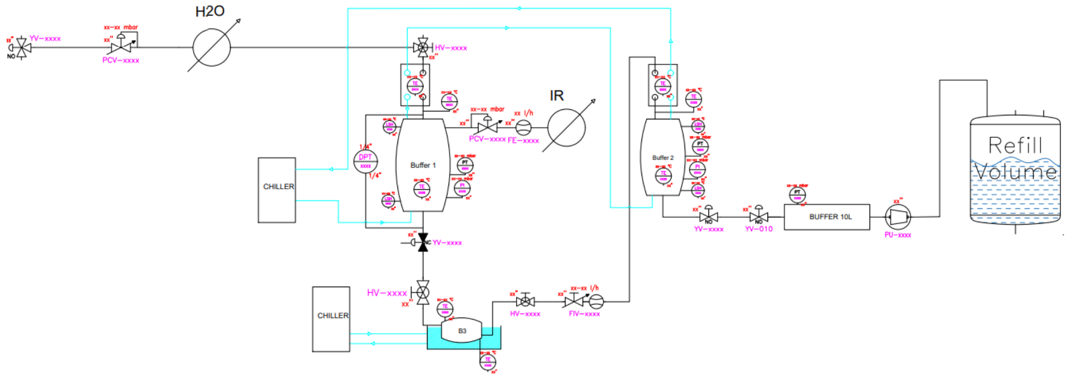


Figure 23: Schematic representation of the first system modified.

The difference between the first version is the addition of one buffer, which it is called “Buffer 3”. It is directly connected to the first Buffer, and it has a different chiller in order to set the perfect temperature for the distillation process. All the process changed. The distillation no longer provides for the liquefaction and subsequent storage of the two gases but has the following steps:

- Liquefaction of the azeotropic mixture in order to eliminate incondensable as air and SF6;
- Distillation process entering into the buffer 3, where the temperature is higher;
- Cooling down to liquefaction point removing the remaining part of the incondensable;
- Storage pure R134a.

Many tests have been carried out over the years with the aim of recovering R134a as pure as possible with optimal efficiency. Since the pressure of the process is set to the atmospheric pressure, it is needed decide the range of the temperature and the time of the process. As shown in Figure 23, the azeotropic point, in which liquid and vapor phase have the same composition is around -32°C. Therefore, the chiller is set in order to maintain the temperature inside the first buffer lower than this value to liquefy the mixture and separate incondensable from the azeotropic mixture. Moreover, the temperature of the "Buffer 3" is relevant, because increasing this temperature can cause a loss of R134a with a consequent reduction of general efficiency of the process. The lastly parameter that is fundamental to consider is the time. Increasing the distillation time decreases the concentration of impurities in the final product. Time and temperature are the two parameter that need to be optimized in order to reach the desired level of efficiency. The following paragraphs will show the results of the first tests conducted with the upgraded version of the system and a brief outline of how the composition of the recovered gas was evaluated.

Brief summary of the tests with updated version of System I

The R134a recovery system has been designed to recover Freon not subject to recirculation, that is, 10% of the 10 m^3 of mixture fed into the RPCs. For this reason, the system must be able to handle a variable flow rate between 0 and 800 l/h, so from the outset it was necessary to test different inlet flow rates in order to optimise the two process variables, temperature and time.

The system configuration provides for the entry of the liquefied mixture into buffer 1, which is in contact with buffer 3 through a manual valve. The valve is kept open so that the distillation process takes place during filling. Increasing the filling speed reduces the distillation time, so that to achieve the same level of gas quality it is necessary to increase the residence time as the filling speed increases. In order to identify the optimal operating conditions that would lead to good gas quality, several tests were carried out, which focused on the temperature of the B3, the filling speed and the holding time. These three parameters play a key role, since in order to arrive at a process that is efficient and as accurate as possible, it is necessary to conduct several tests and study their effects on the system. From the outset, it was noted that the filling time and stationary time are intrinsically linked, so increasing the filling is forced to increase the stationary time. This connection leads us to identify the first limitation of the system. All operations cannot be carried out continuously, so there will be a filling phase, a stationary phase and a final unloading phase. For this reason, all tests carried out relate to a certain volume of mixture relative to the filling time.

Before proceeding to the analysis of the various tests, it is necessary, as previously explained, to carry out a calibration. The best way to obtain an optimal calibration factor is to calibrate with a value as close as possible to the expected value. Calibration is usually carried out by performing analyses with the chromatograph gas from a cylinder containing precise percentages of the components to be calibrated. This operation was performed using a cylinder containing 5% Isobutane and 95% R134a, percentages that correspond to those contained within the RPC mixture. A chromatogram of the mixture is shown in Figure 24 for comparison with the chromatograms shown later for the tests.

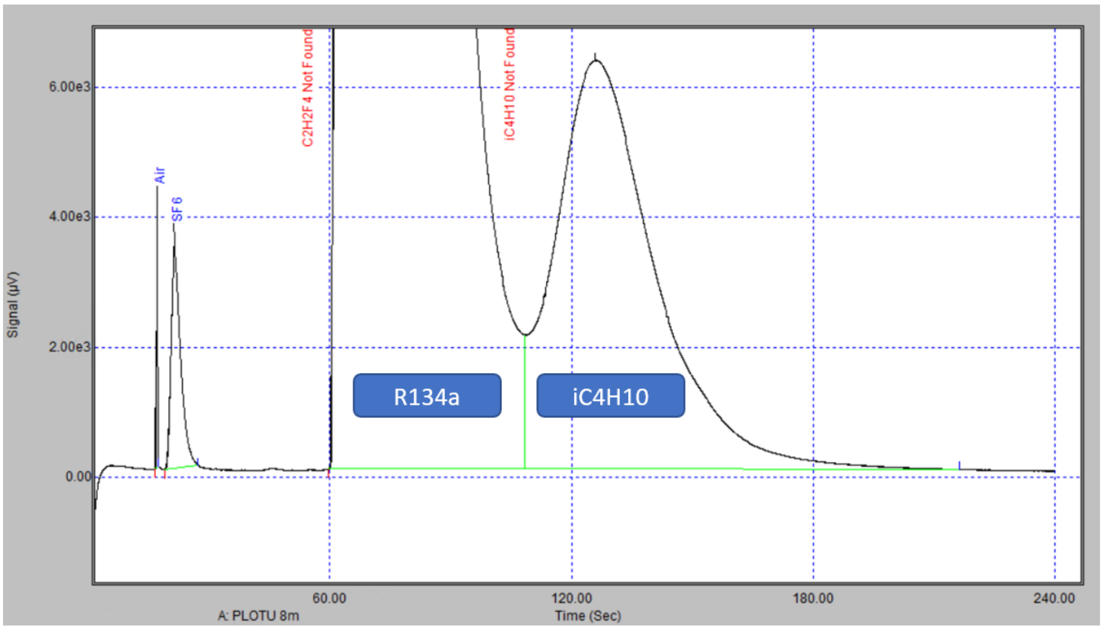


Figure 24: Chromatogram of the RPC mixture in PPU

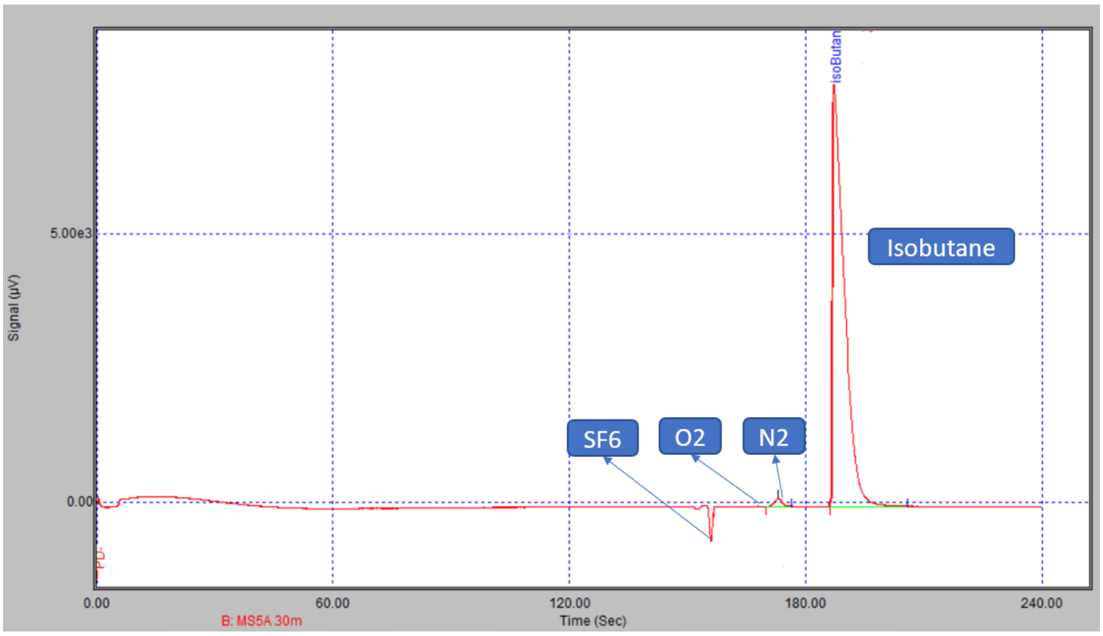
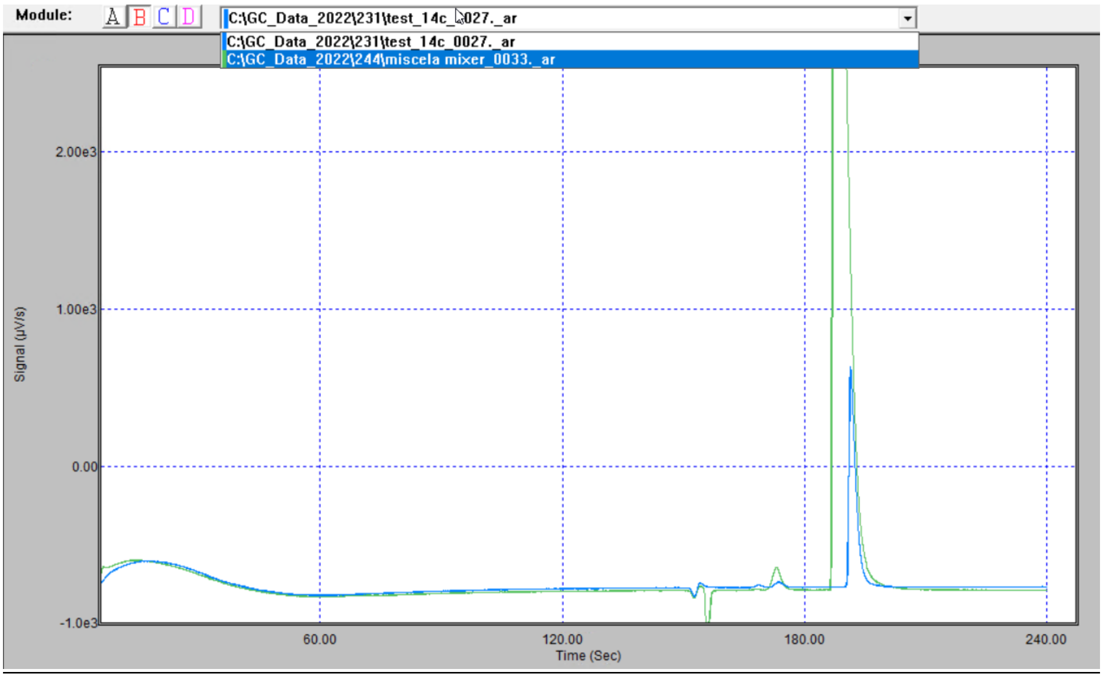


Figure 25: Chromatogram of the RPC mixture in MS

The two images, Figure 24 and Figure 25 show the chromatograms for the PPU and MS column. As can be seen, the indication of the presence of isobutane is present in both. Following various tests and analyses that will not be reported here, only the chromatograms from the MS will be analysed. This is because in the PPU column, although the isobutane peak is clearly visible, integration techniques do not allow the actual area to be estimated correctly. Using the technique of integrating the division of the two peaks tends to overestimate the presence, while integrating along the R134a curve tends to underestimate. This was demonstrated by analysing the mixture of RPCs. After obtaining the chromatograms, and observing all the areas corresponding to both PPU and MS, by means of the known isobutane percentages, it was possible to evaluate a calibration factor. One of the tests was then taken as an example, noting that the percentage of isobutane detected by the PPU is considerably lower than that of the MS.

The tests performed were grouped into two classes based on the temperature set for buffer 3. The two temperatures are 6°C and 9°C. It is expected that for the same filling and standing conditions, the percentage of isobutane is higher when the temperature is 6°C than when it is 9°C degrees.

“TEST 14” , with ‘Buffer 3’ set at 6°C:

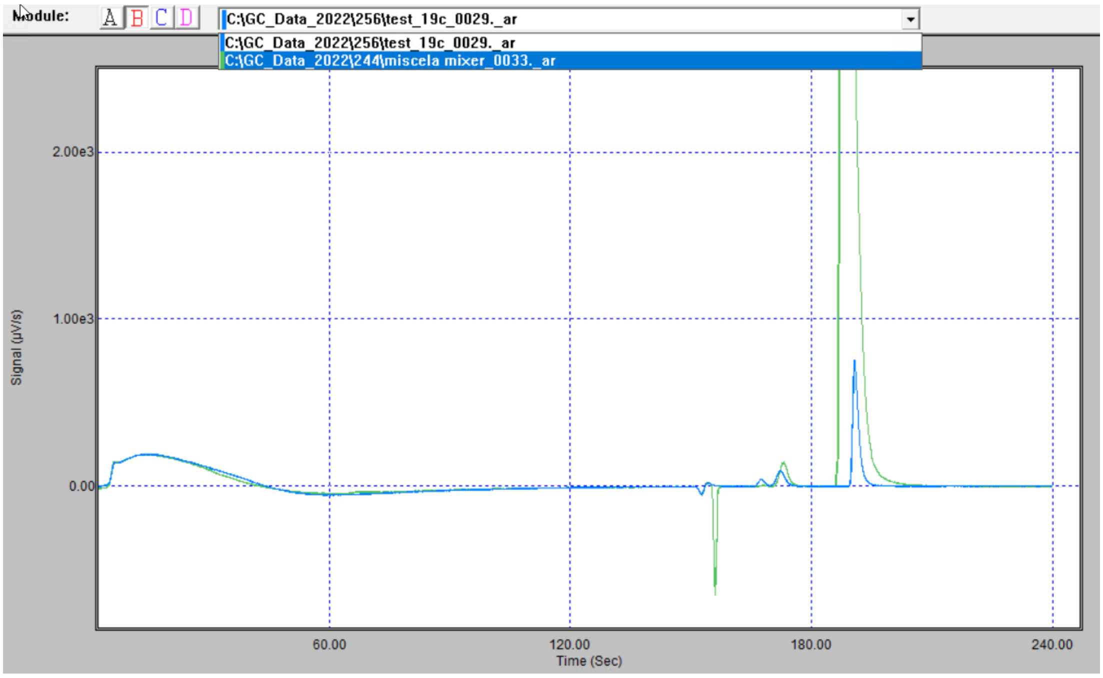

Module: A B C D

C:\GC_Data_2022\231\test_14c_0027._ar

C:\GC_Data_2022\231\test_14c_0027._ar
C:\GC_Data_2022\244\miscela mixer_0033._ar

Figure 26: Comparison Test 14 with RPC’s mixture in MS

TEST 19, with ‘Buffer3’ set at 9°C:


Module: A B C D

C:\GC_Data_2022\256\test_19c_0029._ar

C:\GC_Data_2022\256\test_19c_0029._ar
C:\GC_Data_2022\244\miscela mixer_0033._ar

Figure 27: Comparison Test 19 with RPC’s mixture in MS

By going from a 'Buffer3' temperature of 6°C to 9°C, it is possible to see an improvement from the point of view of isobutane concentrations within the total mixture, which go from 4.51% to 0.4%. These concentrations are realistically low, but not low enough for the recovered freon to be considered a pure gas. This is because the prototype of the R134a recovery will be connected to the mixer, in which it will then be mixed together with iC4H10 and SF6 in the established percentages. If R134a is supplied with iC4H10 already in it, the mixer, not being able to scan in real time, will mix it at the preset percentages, leading to an increase in isobutane.

The area values for each test relative to the isobutane peak are useful for developing the comparison between the two different temperatures. As the area value is not very meaningful, it is necessary to convert it to a value of interest. To provide a reference value, areas are converted back to ppm or %. This is possible thanks to the Calibration Factor. The procedure for obtaining a correct calibration factor is as follows:

- Using the gas chromatograph, analyse the mixture to be analysed of which the exact percentages are known;
- To obtain an extremely accurate calibration factor, the percentages of the gases in the known mixture should be as close as possible to those expected in the final mixture;
- From the chromatogramm, calculate the area relative to the component of interest;
- The calibration factor will be the ratio of the percentage of the component in the known mixture to the area value measured by the chromatogram.

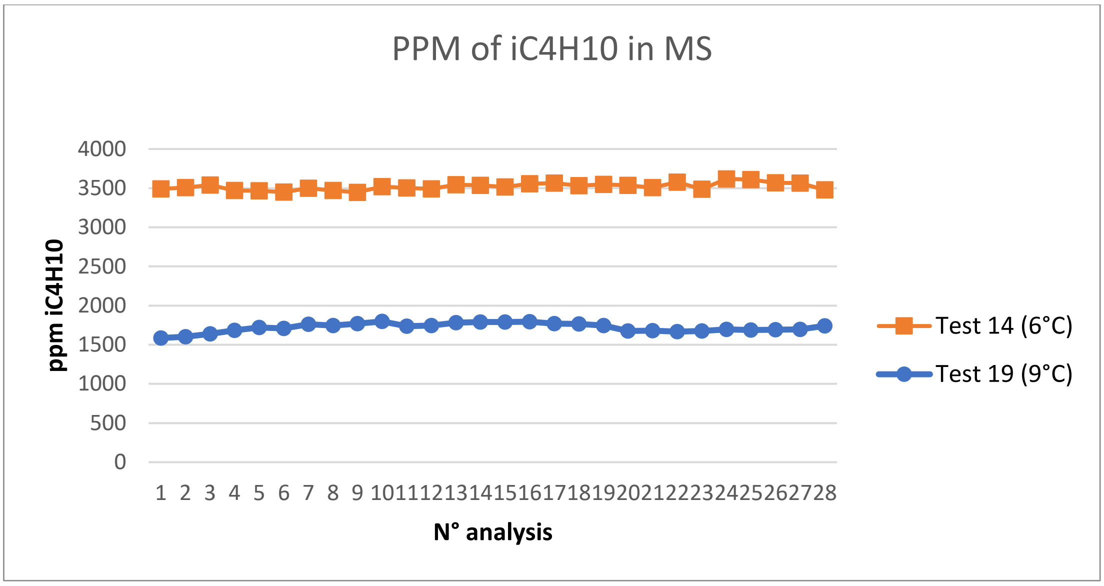


Figure 28: Comparison of ppm concentration in Test 14 and Test 19

The curves are perfectly distinct and far apart, showing how the temperature of 'Buffer 3' greatly influences the concentration of isobutane within the mixture. This set the stage for the next tests to be carried out on the new configuration of the first prototype.

3.3 2^{nd} modification of the Prototype "I"

The first modification of the system therefore led to two mixture phase changes, resulting in a delay on the entire phase. For this reason, as well as only handling the flow in batch, the prototype was not able to handle a high flow. With the new prototype, the objectives are both, work continuously and handle a variable flow rate. Before moving on to the design of the new prototype, it was possible to carry out some tests on the first one, modifying its configuration once again. The tests carried out with this configuration will allow us to identify the criticalities that need to be resolved in the new prototype and the parameters on which to act to optimise the process and increase its efficiency.

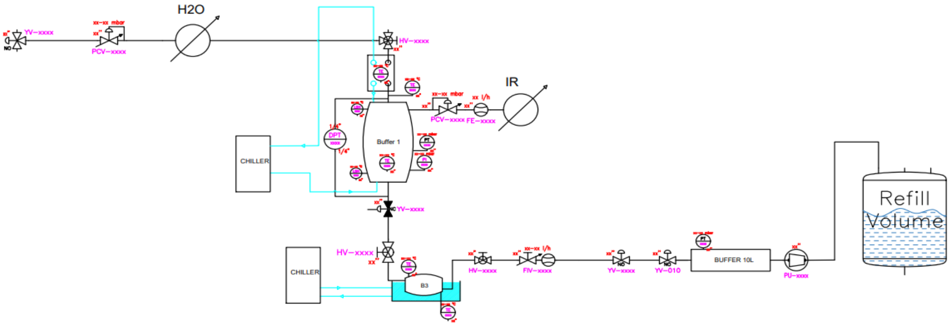


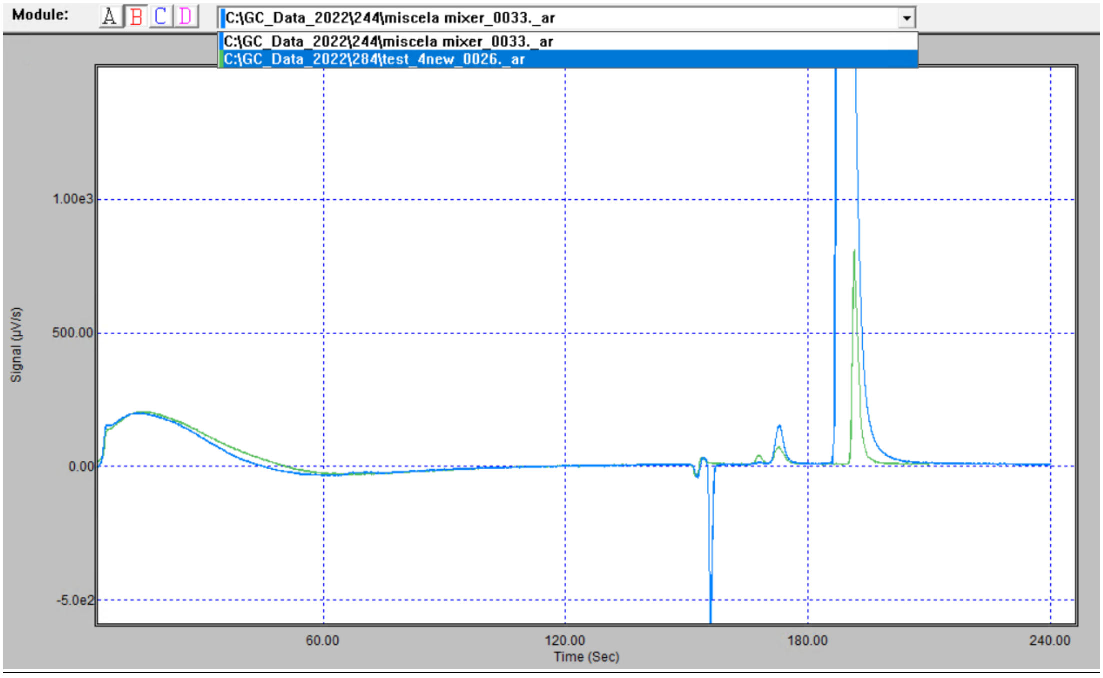
Figure 29: P&ID of the first prototype with the last configuration

Figure 29 shows the 2D of the new modification carried out on the first prototype. It can be seen that all the part preceding 'Buffer 3' has remained exactly the same as before, while the connection made between it and 'Buffer 2' has been removed. At this point the 'Buffer 3' goes directly to 'Buffer 4', the accumulation volume that precedes the compressor and then into the storage tank.

In this way, the gas after being liquefied in the heat exchanger will enter 'Buffer 1' which will be directly connected to 'Buffer 3'. The manual valve downstream of this will be kept closed according to the holding time. As expressed above, the holding time is a key parameter for proper distillation of the mixture. After a set time, the valve is opened, and the compressor switched on. During the storage phase, a slight depression will be created in the system, which will be interrupted by the liquid front in 'Buffer1'.

Tests conducted with this new configuration will tend to evaluate the concentration of isobutane by varying certain parameters of interest, such as the temperature of 'Buffer 3', the filling speed and the dwell time. The temperature parameter always plays a key role in the whole process. For this reason, the tests conducted with this new configuration are also carried out with two temperature levels: 9°C and 17°C.

“TEST 4”, with ‘Buffer 3’ set at 9°C:

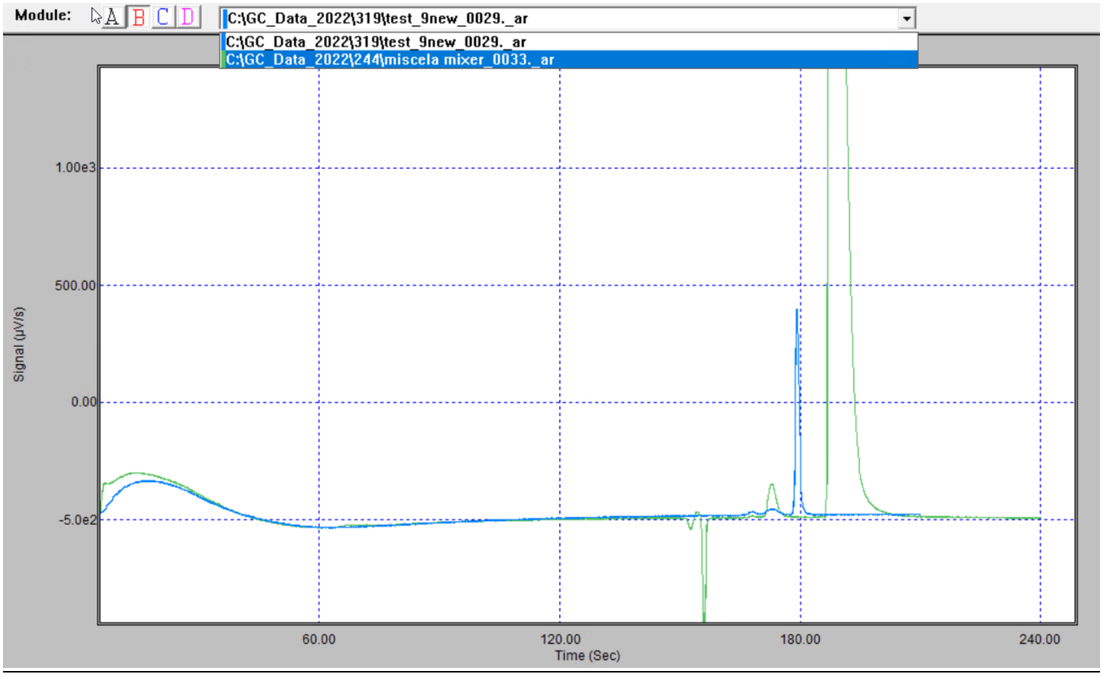


Module: C:\GC_Data_2022\244\miscela mixer_0033._ar

C:\GC_Data_2022\244\miscela mixer_0033._ar
C:\GC_Data_2022\284\test_4new_0026._ar

Figure 30: Comparison Test 4 with RPC’s mixture in MS

“TEST 9”, with ‘Buffer3’ set at 17°C:



Module: C:\GC_Data_2022\319\test_9new_0029._ar

C:\GC_Data_2022\319\test_9new_0029._ar
C:\GC_Data_2022\244\miscela mixer_0033._ar

Figure 31: Comparison Test 9 with RPC’s mixture in MS.

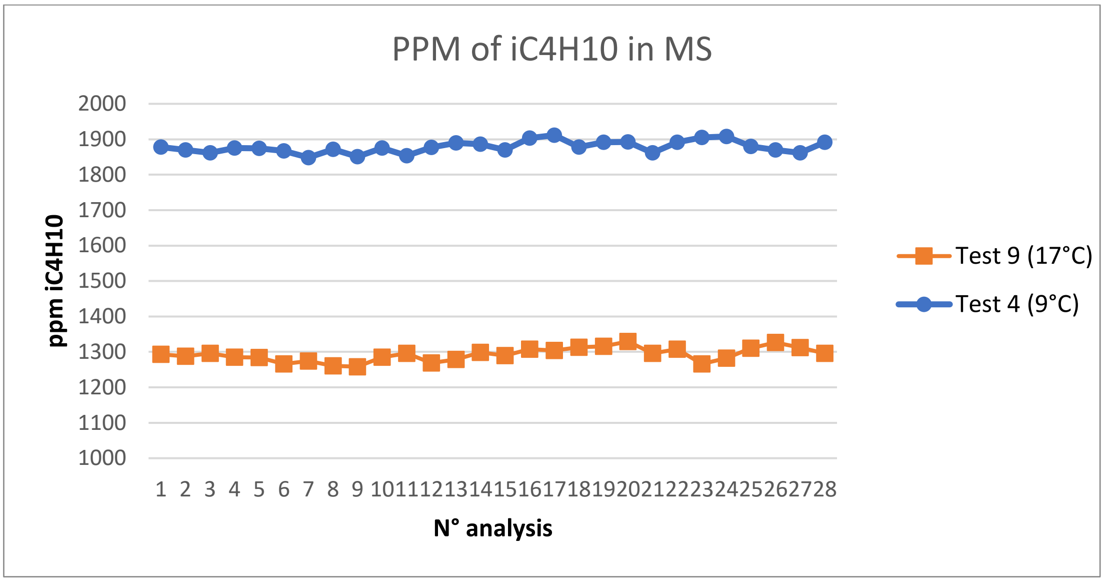


Figure 32: Comparison of ppm concentration in Test 4 and Test 9

The new configuration allows mainly to verify that the second state transition in 'Buffer 2' does not bring any benefit to the recovery since at the same temperature in 'Buffer 3' the isobutane concentrations are the same. Moreover, the temperature increase in ‘Buffer 3’ leads to a drastic reduction in concentration of isobutane, again emphasising the extremely important role of temperature on the entire process. The concentration of isobutane is not yet low enough to store R134a as pure, but it allows us to identify the parameters on which to intervene on the next prototype in order to increase its efficiency.

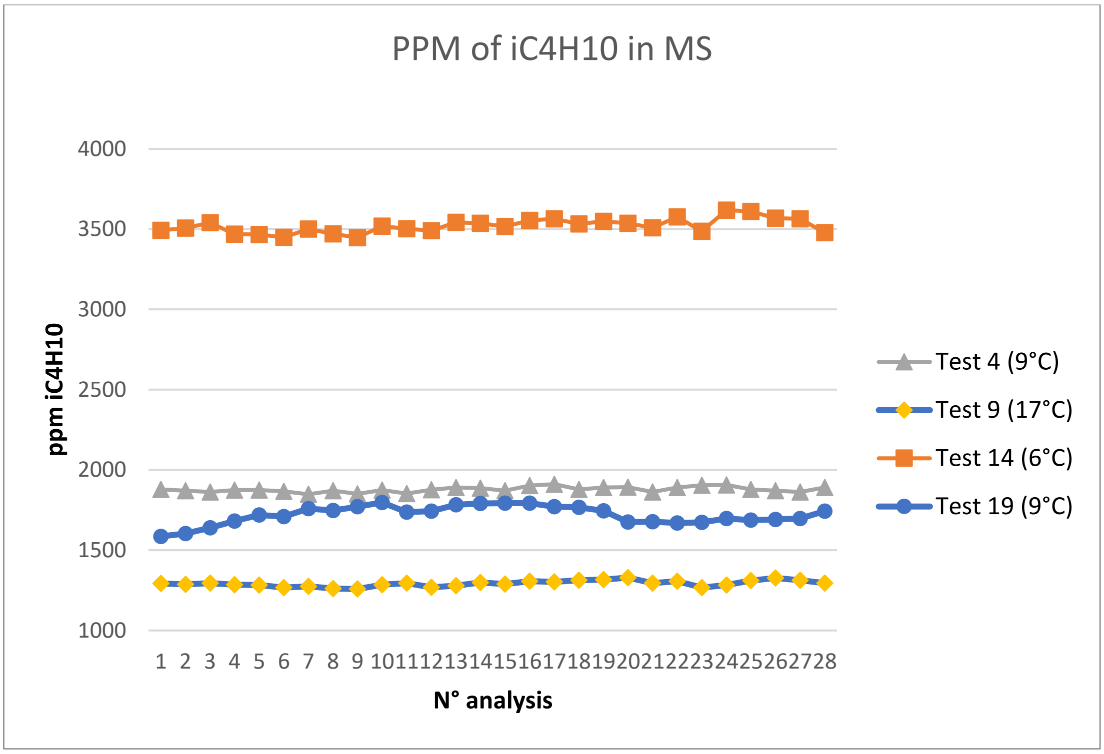


Figure 33: Comparison of the four tests done with the two prototype configurations.

Figure 33 shows the comparison of the four tests conducted, the first two with the old configuration and the last two with the new one. It can be seen immediately that all the assumptions made before conducting the tests have been verified, such as having identified the temperature of 'Buffer3' as a key parameter on which to act in order to reduce the concentration of Isobutane within the recovered gas. In addition, the proximity between test 14 and test 4 is proof that the new configuration, with the by-pass of 'Buffer 2', is the right path on which to design the new prototype. This comparison, therefore, made it possible to eliminate an additional phase change with a consequent waste of energy and time.

4. R134a Recuperation system Prototype “II”

Freon recovery is the main theme of this thesis work. The increasing focus on the issue of climate change makes it necessary to find a solution involving the re-use of the gases used in the RPC mix. As expressed in the previous chapters, the RPC mixture has mainly three gases: Freon, Isobutane and SF6. Each of these if released into the atmosphere contributes to the global warming condition and their relative damage is measured in GWP. This indicator is calculated from CO2, as the GWP takes its meaning by considering the heat absorbed by any greenhouse gas in the atmosphere relative to that which would be absorbed by the same mass of CO2. It therefore depends on the composition of the gas and the time. It is a useful tool for measuring the climatic effects of different gases. R134a has a GWP of 1430, iC4H10 is 3 and SF6 is 22800. Although SF6 is the gas with the highest GWP, it also corresponds to the lowest contribution of the mixture since it is 95% R134a. For this reason, the prototype was designed to fully recover the R134a in order to re-inject it upstream of the mixer and thus reduce both pollution and cost. The cost of injecting fresh mixture into the recirculation circuit is a major contributor to costs. It is estimated that the price for R134a is around 230000 CHF per year per experiment (ATLAS and CMS). In other countries, such as France, it is even doubled due to the lack of availability.[21]

With Prototype ‘I’, it was possible to study the evolution of the mixture at the various transformation stages, determining the azeotropic mixture and the resulting limits. Over time, different configurations of the system were used to optimise energy consumption, but above all the efficiency of the system and the quality of the recovered gas. The latter is a fundamental point, since in order to be able to inject the recovered Freon into the mixer, it is necessary to know the composition of the gas being sent with extreme precision. The operating principle of RPCs is based on the correct composition of the gases within them. This is why the mixer, starting from pure gases, provides the correct concentration of the desired gases. Once it is certain that the recovered freon is almost pure, it can be sent to the mixer.

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[21] F. Cambiè “R134a separation and recuperation from the gaseous mixture used in the Resistive Plate Chamber detectors at the CMS Experiment”, Geneve, CERN, 2021

The path the mixture takes ends at the outlet of the RPC chambers where 90% is recirculated, while 10% is released into the atmosphere. The freon recovery system aims to recover the R134a contained in that 10 % and reuse it as fresh gas. To fulfil this purpose, it is necessary to manage the flow from the exhaust and this involves developing a system that can work continuously. All previous tests had been carried out in batch, which involved loading phases interrupted by stationary phases in which the mixture could separate. The new prototype has been designed so that recovery can take place continuously.

4.1 Design of the Prototype “II”

Figure 34 shows the P&ID, Piping and Instrumentation Diagram, of the new prototype based on the experimental data collected with prototype I following the latest modifications. The design of the system comes from the need to handle variable flows from the exhaust, which is why a modular design was chosen.

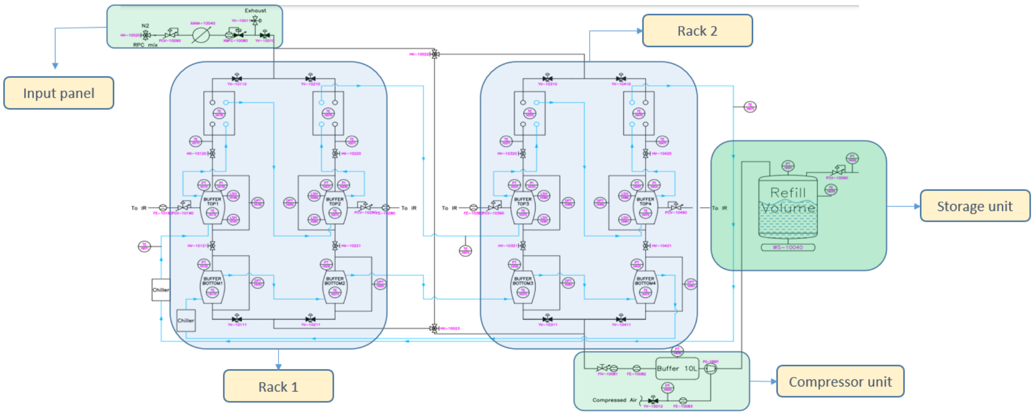

Figure 34: P&ID and conceptual grouping of prototype “II” components

The figure 34 conceptually highlights the geometric division of the various spaces. It is possible to see the two separate racks in blue, and all components housed outside the racks in green. Starting from the left, the rack containing the plc and all the components required for the input of the mixture from the RPC exhaust has been positioned. This is followed by the first modular rack, which is then repeated in the second. Next is the compressor unit located in a special soundproofed cage and finally the storage unit.

4.1.1 Input panel & Electrical rack

The first rack is used to house electrical and electronic components. It provides for the proper functioning of the system through the PLC (Programmable Logic Controller) and all actuators connected to it. The operating principle will be explained later. In addition, the first rack houses all components necessary for inputting the mixture into the system.

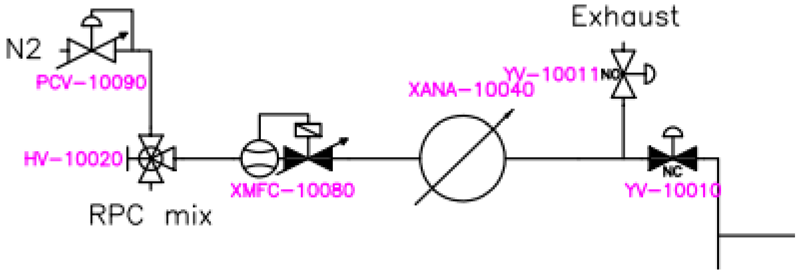

Figure 35: Input panel

In Figure 35 you can see:

- the first three-way valve (HV-10020) which allows the system to be connected to both the mixture exhaust from the RPC and a nitrogen line. This is because under maintenance conditions or for any modifications to the system, it is necessary to purge the system before opening the gas circuit. This step is of fundamental importance as the gas room in which the system is located contains i-C4H10 detectors and, as isobutane is a flammable gas, it is necessary to ensure that it is not released in a confined environment;
- The mass flow controller (XMFC-10080), which regulates the flow through the system. Under normal operating conditions, the mass flow will only manage the maximum permissible flow in the system. This is because as the exhaust flow is variable, the system will be dimensioned for a maximum flow,

which can be increased by adding more modules. In the test phase, on the other hand, it will be possible to determine the inlet gas quantity via the mass flow;

- The humidity sensor (XANA-10040)is an essential instrument for observing in real time how much humidity is contained in our mixture. The instrument is equipped with two electrodes and a metal oxide layer. The passage and amount of vapour, absorbed by the layer changes the capacity between the electrodes proportionally;[22]
- The two pneumatic valves (YV-10010/YV-10011). They are, according to P&ID language, one 'normally closed' and the other 'normally open'. This is because they correspond to the safe positions, those positions that the two valves must have in STOP or emergency conditions. In particular, the valve connected to the exhaust is 'normally open', so that it can isolate the system in the event of danger, and therefore the other is 'normally open'.

4.1.2. Inside the 1^{st} Rack

The two racks have the same configuration, so the development and construction of the first rack will be analysed in detail. The need to handle the flow from the continuous exhaust led to the design of a rack containing two separate columns. Both columns perform the same function, operating in batch but with the full flow coming from the exhaust.

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[22] "Dew point sensing technologies and their performance differences in compressed air applications" https://www.vaisala.com/sites/default/files/documents/VIM-GLO-IND-HUM-Dewpoint-sensing-technologies-App-note-B211092EN

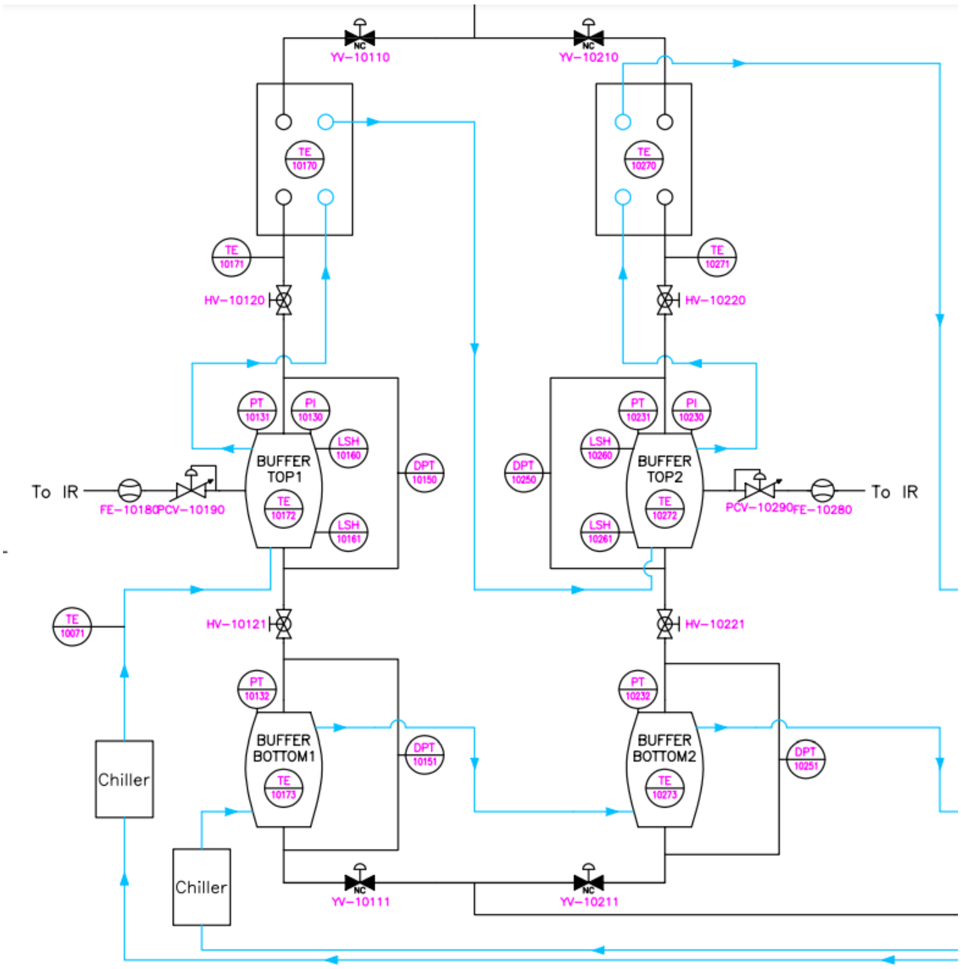

Figure 36: P&ID of 1st rack

The P&ID of the first rack is useful to understand the modularity of the freon recovery system. Depending on the input flow to be handled, the columns and racks must be correctly dimensioned. Considering a given input flow, it is possible to size the system, providing a filling time, a stationary time in which the distillation of the two components takes place, and finally a discharge phase, and then repeat the procedure in order to maintain a constant input flow into the freon recovery system. Should the flow increase, the system sized for a lower flow will not be able to handle the new flow, which is why the modularity of the system offers a great advantage. It is sufficient to add a rack with more columns inside it. This will increase the capacity of the entire system.

In order to better understand the operating principle, the first rack will be analysed in detail starting with the individual columns that make it up. One being will be sufficient to fully describe the system as the columns contained in a rack are identical.

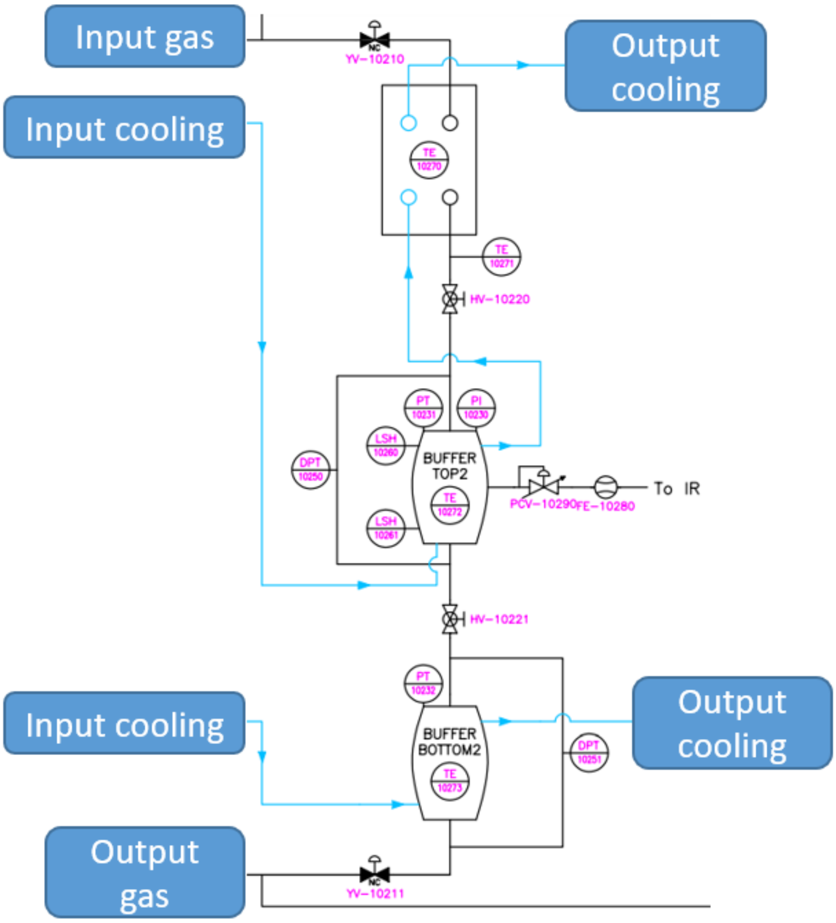

Figure 37: Schematic representation of one Column of the 1st Rack

Figure 37 shows the detail of one of the two columns in the first rack. It can be divided into the gas side and the cooling side. The former takes into account the passage of gas and then liquid from the mixture coming from the RPC, while the latter is responsible for the cooling of the various phases. The mixture from the RPC, which has already passed through the input rack, begins its journey through the first pneumatic valve which connects the system input to the heat exchanger. At this point, the mixture reaches a temperature of -36°C and becomes liquid. The passage connecting the heat exchanger to Buffer 1 can be interrupted by a manual valve in the event of maintenance. Inside Buffer 1, a temperature of -36°C is maintained by the same refrigerant flowing through the heat exchanger. This is possible due to the special geometry of Buffer 1, which will be shown in detail later. The buffer was equipped with a number of useful instruments to measure and control the state of the mixture inside, such as the DPT which measures the liquid level through differential pressure, the two ON/OFF (LSH) level sensors useful when programming the PLC, and the pressure and temperature sensors for monitoring. From Buffer 1, an exhaust line is provided through which the gas phase of the mixture is expelled. Following the liquefaction of the mixture in the heat exchanger, freon and the azeotropic mixture are in the liquid phase, while air and SF6 remain in the gaseous phase since their liquefaction temperature is even lower.

Following the distillation phase, the gas phase will be enriched with the azeotropic mixture, leaving only R134a in the liquid phase. The connection between Buffer 1 and Buffer 3 is made by means of a manual valve, again useful during maintenance. It is at this point that the actual distillation takes place. The liquid formed in the heat exchanger and then in Buffer 1 arrives in Buffer 3, which is set at a much higher temperature than Buffer 1 and the heat exchanger by using a second chiller. At this temperature, the mixture of freon and azeotropic mixture will no longer be in a liquid state but will evaporate as it travels back down the pipeline to buffer 1. There, the evaporated mixture will come into contact with a mass of liquid cooled to -36°C. The freon, having a liquefaction temperature of -26°C, will return to the liquid phase, resuming the cycle, while the azeotropic mixture, having a liquefaction temperature of -32°C, will leave the exhaust line of buffer 1. In order for the entire mixture to be depleted of the azeotropic mixture, it is necessary to wait a certain amount of time, after which the pneumatic valve following Buffer 3 will be opened, and the line being under vacuum, the now pure R134a gas will be conveyed through the compressor into the storage tank.

4.1.3 Compressor & Storage Unit

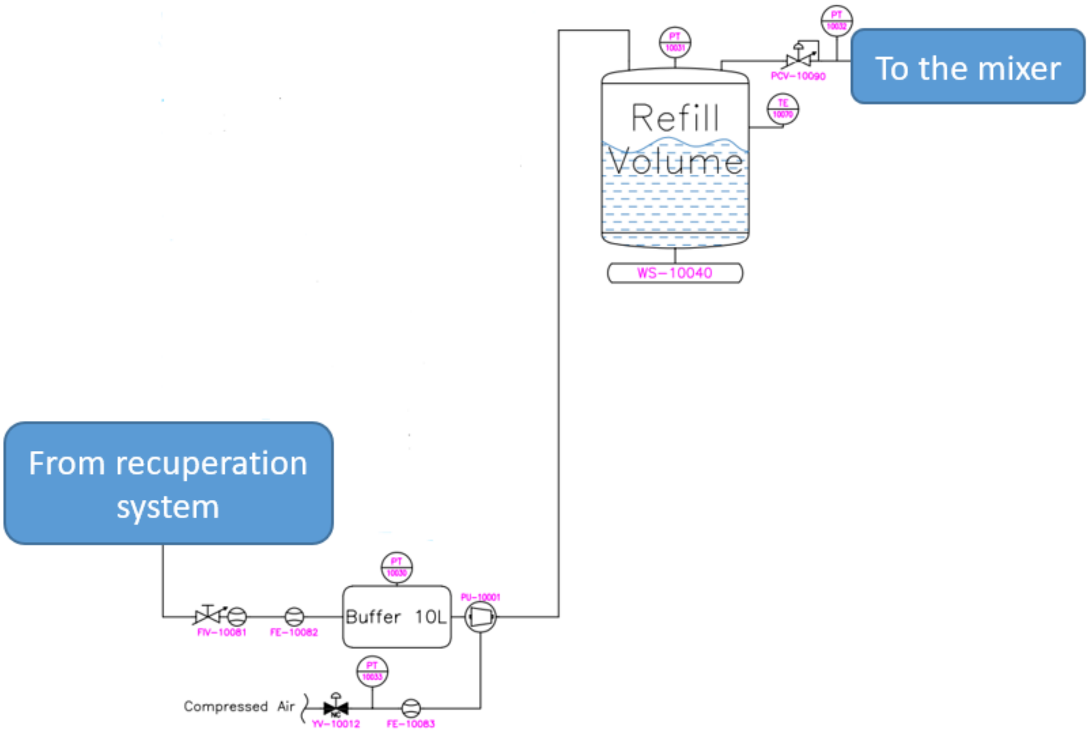

Figure 38: Schematic representation of the storage and Compressor

The gas from the columns contained in the racks passes through a rotameter, which can regulate its flow, before entering the storage volume in front of the compressor. There is also a flow readout on the line, which is used to check the actual operation of the compressor. It works with potentially flammable gases and is a compressor driven by compressed air. There is a pneumatic valve on the line that represents the ON/OFF condition of the compressor, and also a flow meter so that it can check if it is working properly.

The compressor compresses the gas in a storage tank which is monitored by pressure and temperature sensors, since at room temperature l R134a tends to liquefy around 5 bar. If this pressure is exceeded it means that air is also compressed inside the storage volume. In addition, there is a scale under the tank thanks to which it is possible to weigh the weight gain continuously and be able to compare it in real time with what has been input to the system. This allows to have a measure of efficiency of the entire system.

4.1.4 CATIA V5, 3D design

A fundamental step for the development of the recovery system is the 3D design related to the racks. Since the racks are identical, it was possible to represent only one and then duplicate it during construction. The study that is behind the 3D design of a rack, as in this case, must take into account many aspects related to geometry. In fact, it is necessary to consider:

- The optimization of the spaces;
- The position of some components that cannot be changed, such as the flammable gas detection, obligatorily positioned at the bottom since R134a and iC4H10 are heavier than air;
- Correct dimensions and space for the insulation. It occupies most of the internal volume of the rack, so it is a very important parameter to take into account;
- Convenience in the assembly and disassembly of the rack, as well as during the maintenance phases.

The latter is a fundamental parameter since any system or component must be designed to be easy to use. Even more so an experimental prototype like this which could be subject to numerous changes over time.

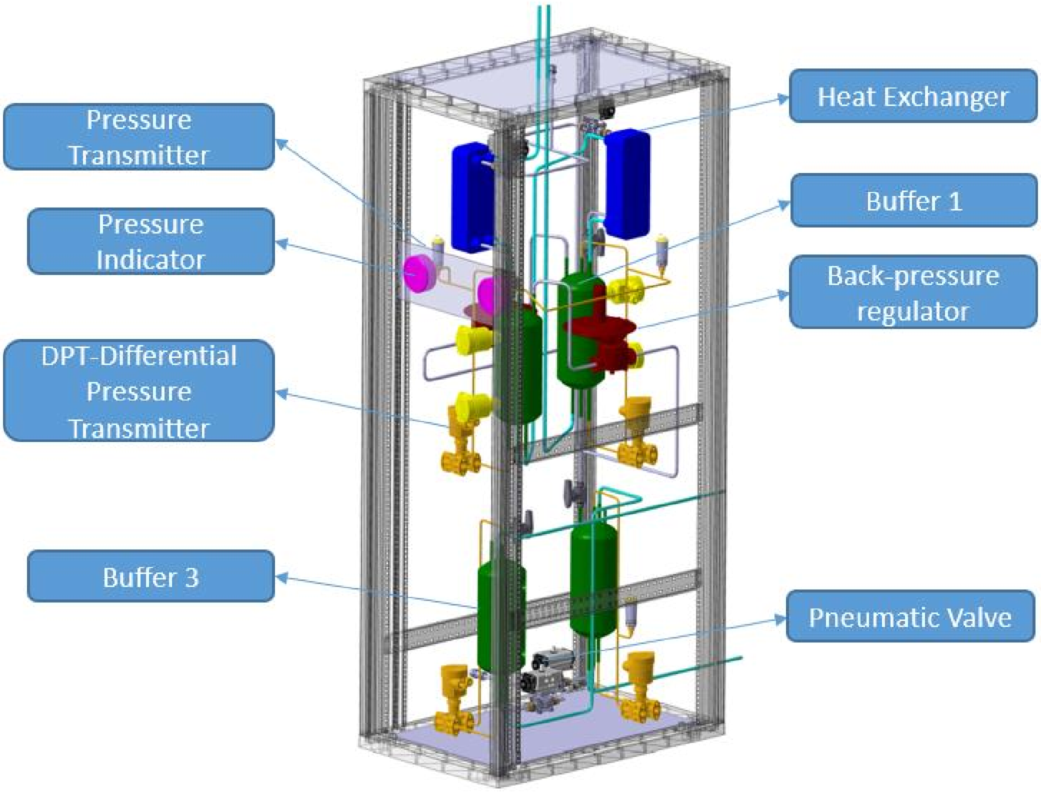

Figure 39: 3D design R134a recuperation Prototype "II"

4.2. Prototype construction & leak tests

This section will analyse all aspects from design to the actual realisation of the prototype. The P&IDs, together with the 3D representation, provide the guidelines for the construction of the prototype, which will nevertheless present its own criticisms. All production processes took place in the workshop inside CERN, which has all the necessary tools for the realisation of numerous systems and installations. In the workshop, all the distribution, exhaust, mixer, pumping and analysis racks are manufactured on behalf of the gas team. Furthermore, being a specialised workshop, the technicians, who are also specialised, can carry out works on specific commissions, such as the recovery of R134a. Everything was carried out in-house, except for components such as valves, sensors and heat exchangers. The latter is an important aspect because, as will be analysed later in this section, critical issues arise in the assembly phase, and having the possibility of being responsible for the construction also provides the possibility of finding solutions to any problems that may arise. It is on the basis of these premises that we will analyse all the steps involved in the construction of the prototype which can lead to criticism.

4.2.1 Buffers Volumes

The R134a recovery system mainly consists of buffer volumes, what have been called buffer 1 and buffer 3 in the previous chapters, heat exchangers, pipes and all components such as sensors and valves. In addition, the whole is connected by connections which may be "VCR" which stands for Vacuum Coupling Radiation and "Compression Fittings" which are made by two compression rings that are tighted around the tube.

The volumes, called 'Buffer 1' and 'Buffer 3', have the same geometry, although different dimensions. They are designed so that the liquefied gas from the heat exchangers is stored inside while maintaining the same temperature. For this reason, they have been realised using two concentric cylinders in which the outer one accommodates the same refrigerant as the heat exchanger, while the inner one accommodates the liquefied gas. In the Figure 40 is shown the 2D CAD design of the buffers. The only aspect that changes from one to another is the wheelbase distance. There are 3 types of these volumes with 30 cm, 20 cm and 10 cm of wheelbase.

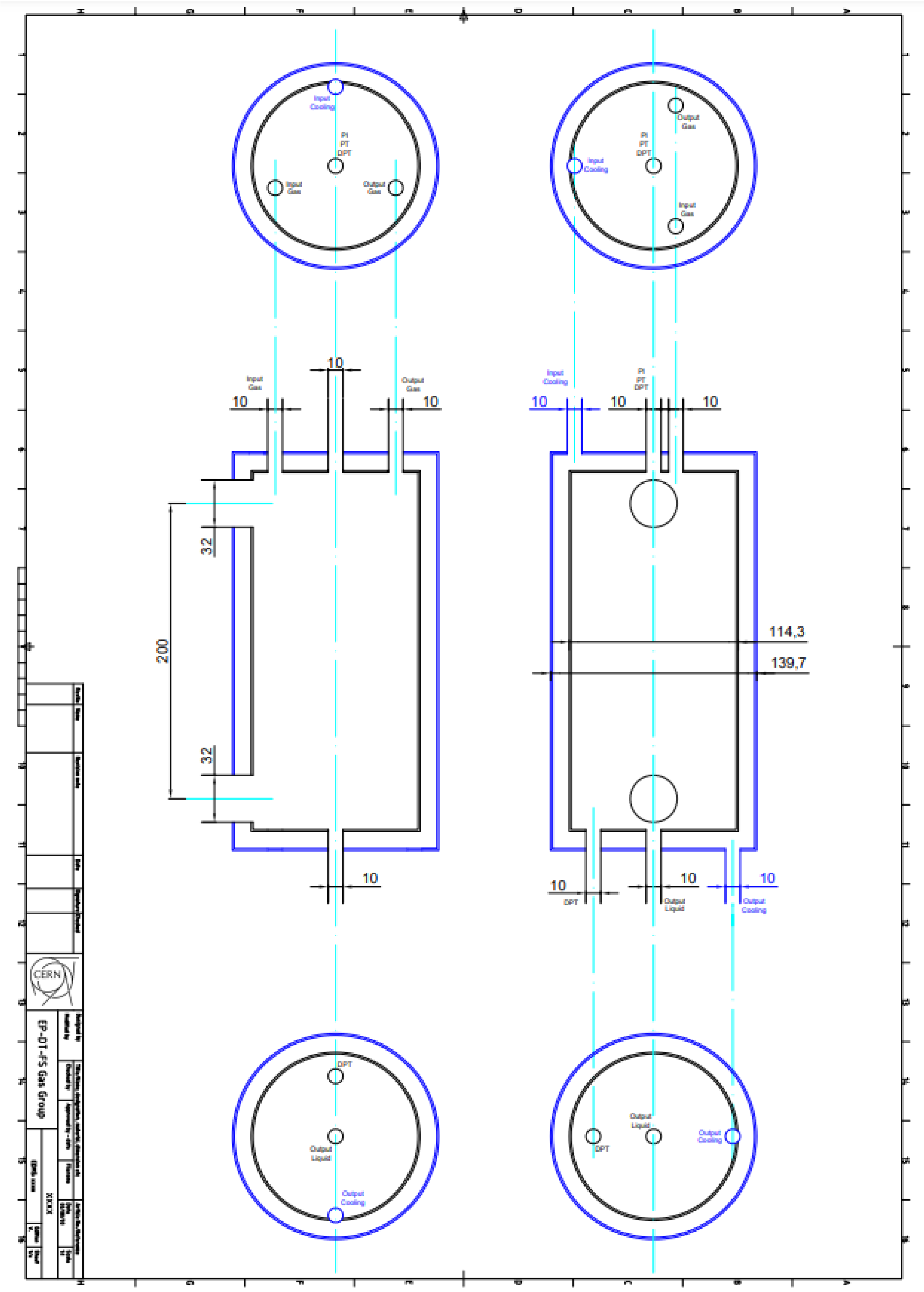

Figure 40: 2D CAD representation of the Buffer volumes

The construction phase of the volumes is the one in which the greatest criticism arises because their construction involves numerous welds, and any one of these, if not performed correctly, can lead to gas or liquid leakage. We start with the first volume to which circular holes are cut on one side which will serve as a housing for the level sensors. Then 4 holes are drilled at the top of the volume and 3 at the bottom to which pipes are welded. The tubes at the top will correspond to:

- Gas input;
- non-condensable gas exhaust;
- pressure sensors;
- cooling output.

While the 3 at the bottom:

- liquefied gas output;
- pressure sensors;
- cooling input.

In Figure 41 it is possible to see the inner cylindrical volume with the holes for the level sensor housings and the tubes described above.

Figure 41: Inner volume of the buffer

Once the inner part has been completed, it is possible to proceed to the outer volume. This is made from a cylindrical sheet in which the holes on the side correspond to those of the inner volume. Next, the two previously drilled covers are welded in correspondence with the tubes that are to come out of the outer cylinder, except for the cooling tubes that are not present in the inner volume but will be welded later in correspondence with their holes.

In Figure 42 you can see the complete buffer, which has the holes for housing the level sensors and tubes described above.

Figure 42: Outer volume of the buffer

4.2.2 Connectors & Welding

All connections between the pipes of the R134a recovery system are made via VCRs or Compression Fittings. The technical difference between the two is mainly the application, as the former are used in more critical operating conditions and are more efficient than Compression Fittings for this reason. In the prototype, they are not strictly necessary, as they work with pressures that are almost ambient, but the usefulness of having a VCR connection in certain positions is that, in order to dismantle or assemble two tubes or two components, it is not necessary to move the two apart or bring them closer together, as in the case of the Compression Fittings, but the female and male nuts are tightened together, creating the connection. Figure 43 shows the VCR connectors in more detail.

Figure 43: Picture of a VCR connector with male and female nuts, the two head and the silver gasket.

Special VCR heads are welded to the tips of the two tubes. A gasket made of a soft metal coated in silver is inserted in the middle. When the nut is tightened, the two welded heads are pressed together, making a groove in the gasket. This step is very delicate as a scratch on the gasket can cause a large leak.

Instead, double bague connectors have the great advantage of being much more practical in assembling different components. The convenience lies in the fact that there is no welding, but the tube is inserted inside a female nut containing two rings, one of which is conical. During assembly, it is sufficient to tighten the nut correctly and the two rings are pressed around the tube until they adhere perfectly.

The critical part for double bague is the fact that if the tube, in the area whose two rings are tightened, neither perfectly smooth, or if is tighted the nut excessively there will be leaks from the connection. In Figure 44 will be shown a double bague connection, highlighting the two rings and the nut.

Figure 44: “Compression Fittings” connector.

4.2.3 Leak Tests

After having analyzed in detail the most critical aspects of the prototype and highlighted the points where leaks of gas or liquid may occur, it is necessary to carry out a series of checks on the correct conditions of functioning. The leak test is a fundamental phase for the realization of the prototype, since after it has been verified that the system does not present any leakage it is possible to proceed with the isolation of all the components and with the electrical connections. Finding a leak after these steps would lead to considerable problems.

Leak tests are conducted through a dedicated set-up. In the case of the R134a recovery system, since there were two racks to be tested, two identical set-ups were made. The operating principle of a leak test is to pressurise all the components to be analysed and evaluate any leaks the system may have. The pressure sensors used are 4..20 mA pressure transmitters which require a special system to read them. A 'yocto-puce' 4..20mA signal reader was therefore used, which via the two input channels of the two pressure sensors directly transfers the data to a database from which a dedicated software extracts and plots them in a time-dependent diagram. The diagram of the trend of pressure over time is fundamental because it allows you to collect data and have a trace of them, monitoring the trend in real time or delayed. In Figure 45 is shown the set-up to read the signal of the pressure sensors. You can notice the pressure sensors, one for rack, the signal reader 4. 20 mA and the computer contains the data plotting software.

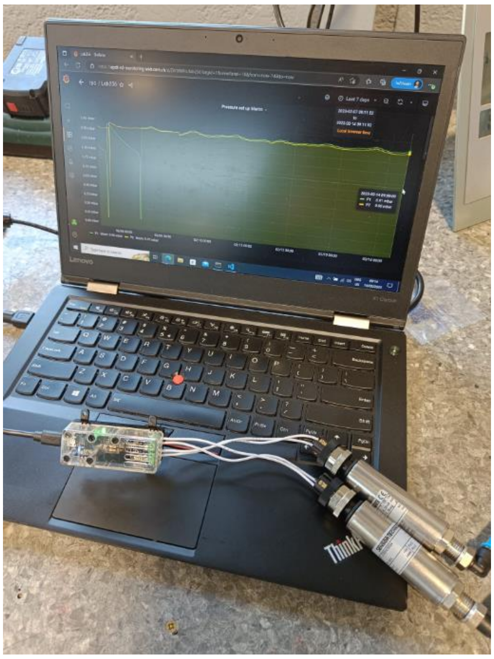

Figure 45: PC, signal reader 4..20 mA and pressure sensors for the two racks

The data obtained with the leak test set-up provide the basis for calculating the system's leak rate. This is a fundamental parameter for determining whether the prototype in question is leaking. This is also carried out by considering other parameters that influence the pressure pattern within the system such as ambient pressure and temperature. Ambient pressure plays a key role since the sensors used are not absolute sensors but provide a value that is influenced by ambient pressure. This is because the operation of the pressure transmitter involves a membrane where one side is in communication with the external environment, while the other side is affected by the pressure inside the system. The variation of the latter sends analogue signals on a 4..20 mA scale, which in turn are converted and finally read out in digital numeric form. The formula used to calculate the leak rate is that for perfect gases, which can be converted and applied to the case under consideration. In order to obtain equation 1, it is necessary to calculate the difference in the number of moles and then convert it to a volumetric flow rate, dividing by time.

Equation 1

$$Q_{LR} = \frac{V * \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) * T_S}{P_s * \Delta\mathrm{t}}$$

V =: Free volume of the device;

T_S =: 273 K temperature at STP conditions;

P_1 =: Absolute Pressure at the start (after stabilization time);

P_s =: Absolute Pressure at STP conditions;

P_2 =: Absolute Pressure after time Δt;

T_1 =: Temperature at the start in Kelvin;

T_2 =: Temperature after time Δt in Kelvin;

Δt =: Time interval.

Being in different conditions than STP, it is necessary to reconvert it. This is why it is possible to use the Hagen-Poiseuille formula considering laminar flow for small losses. It allows the value obtained to be rescaled with the square of the difference in pressures. The end result will be a leak rate expressed as a volumetric flow rate in STP.[23]

Equation 2

$$Q_{LR_{STP}} = Q_{LR} * \frac{P_{0,abs}^2 - P_{0,amb}^2}{P_{1,abs}^2 - P_{1,amb}^2}$$

$Q_{LR_{STP}}$ =: Leak rate at STP conditions;

$P_{0,amb}$ =: Absolute pressure at STP conditions;

$P_{0,amb}$ =: Ambient absolute pressure at STP condition;

$P_{1,abs}$ =: Absolute pressure at the start of the test;

$P_{0,abs}$ =: Ambient absolute pressure at the start of the test.

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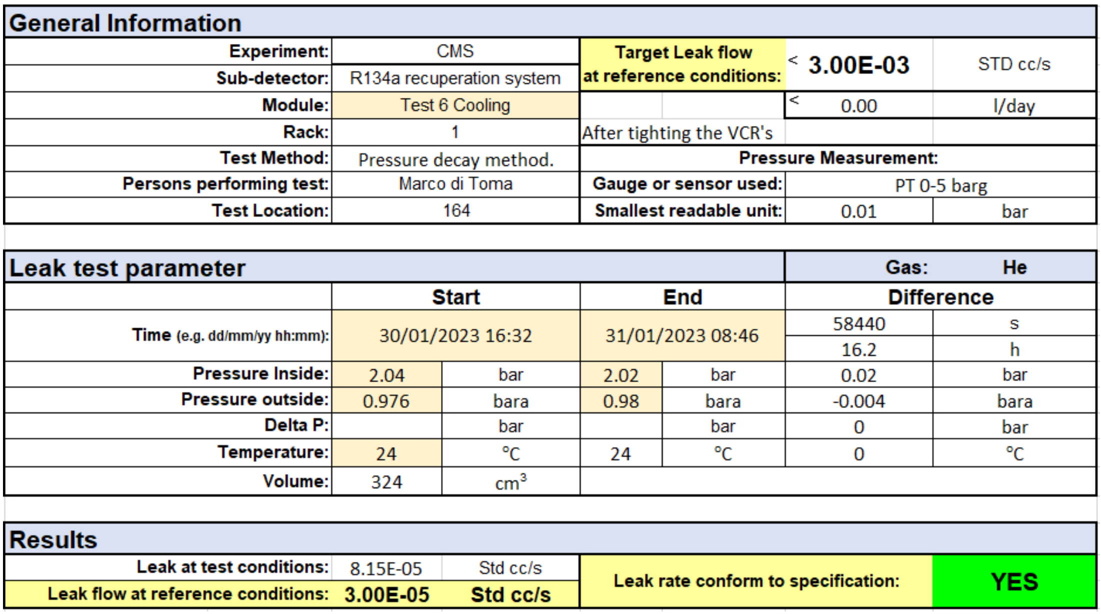
[23] F. Hahn "Guideline for gas rack Leak Testing", Geneva, CERN, 2021

This is summarized in a table which, by comparing the result with a reference value, provides an indication of the presence of leakage. The result gives a quantitative indication of the leakage, which is why it is good practice to deviate from the reference value by at least 1 order of magnitude. In Table 2 shown below we refer to 'leak rate at reference condition' after rescaling the previous value based on pressure.



General Information

Experiment:	CMS	**Target Leak flow at reference conditions:**	< **3.00E-03**	STD cc/s
Sub-detector:	R134a recuperation system			
Module:	Test 6 Cooling		< 0.00	l/day
Rack:	1	After tighting the VCR's		
Test Method:	Pressure decay method.	**Pressure Measurement:**		
Persons performing test:	Marco di Toma	**Gauge or sensor used:**	PT 0-5 barg	
Test Location:	164	**Smallest readable unit:**	0.01	bar

Leak test parameter

					Gas:	**He**
	Start		**End**		**Difference**	
Time (e.g. dd/mm/yy hh:mm)**:**	30/01/2023 16:32		31/01/2023 08:46		58440	s
					16.2	h
Pressure Inside:	2.04	bar	2.02	bar	0.02	bar
Pressure outside:	0.976	bara	0.98	bara	-0.004	bara
Delta P:		bar		bar	0	bar
Temperature:	24	°C	24	°C	0	°C
Volume:	324	cm^3				

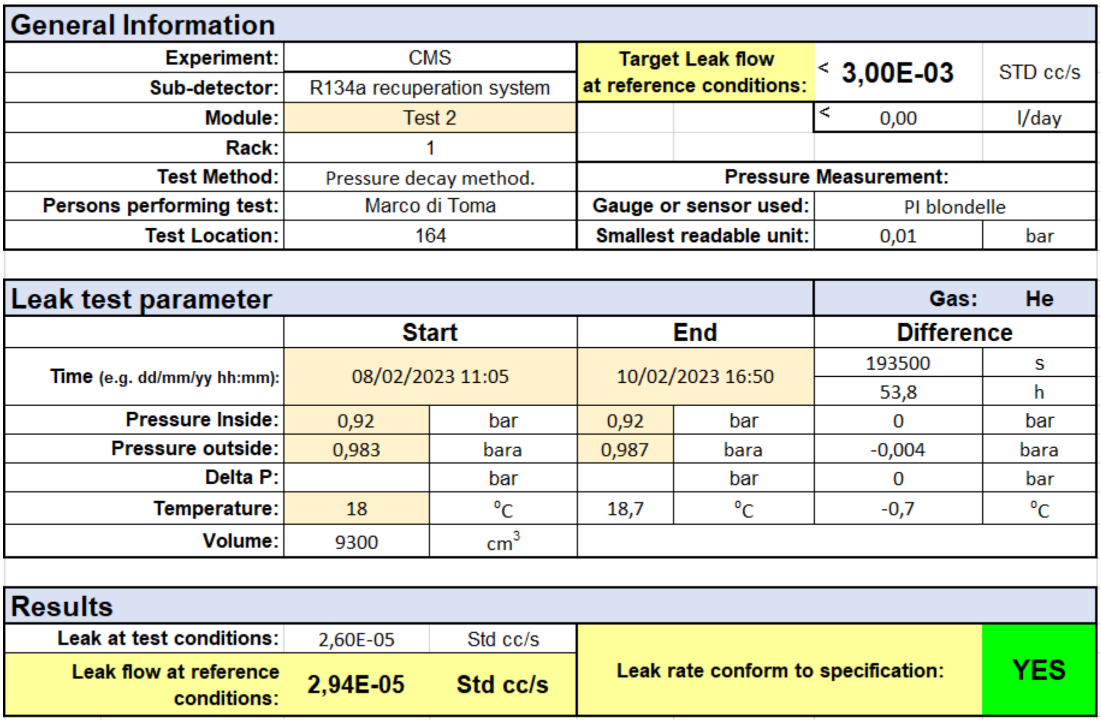
Results

Leak at test conditions:	8.15E-05	Std cc/s	**Leak rate conform to specification:**	**YES**
Leak flow at reference conditions:	**3.00E-05**	**Std cc/s**		

Table 2: Leak test of cooling side

Table 2 shows the result of the leak test calculations performed for the cooling side of the system. Testing the cooling side is an essential step, as the buffers have a concentric geometry and could leak by connecting the liquefied gas side with the cooling side. This could present considerable problems by mixing the liquefied gas with the liquid used for cooling, compromising the entire R134a recovery system.

The part of the system relating to the passage of gas first in gaseous form, then in liquid form and then again in gaseous form presents many criticalities due to connections, buffers and sensors. This is why leak tests are extremely detailed and time-consuming. In Table 3 and Table 4 the latest leak tests performed for both racks are shown, showing that they are leak-free.

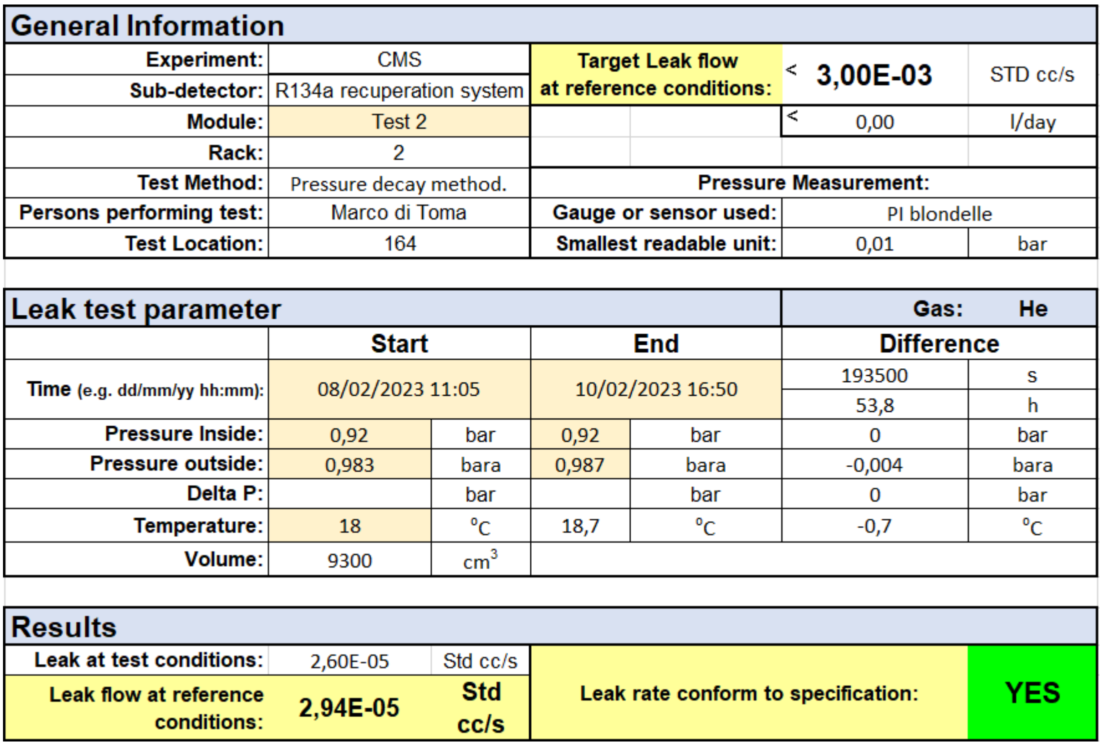


General Information				
Experiment:	CMS	Target Leak flow at reference conditions:	< 3,00E-03	STD cc/s
Sub-detector:	R134a recuperation system			
Module:	Test 2		< 0,00	l/day
Rack:	1			
Test Method:	Pressure decay method.	Pressure Measurement:		
Persons performing test:	Marco di Toma	Gauge or sensor used:	PI blondelle	
Test Location:	164	Smallest readable unit:	0,01	bar

Leak test parameter					Gas:	He
	Start		End		Difference	
Time (e.g. dd/mm/yy hh:mm):	08/02/2023 11:05		10/02/2023 16:50		193500 53,8	s h
Pressure Inside:	0,92	bar	0,92	bar	0	bar
Pressure outside:	0,983	bara	0,987	bara	-0,004	bara
Delta P:		bar		bar	0	bar
Temperature:	18	°C	18,7	°C	-0,7	°C
Volume:	9300	cm^3				

Results				
Leak at test conditions:	2,60E-05	Std cc/s	Leak rate conform to specification:	YES
Leak flow at reference conditions:	2,94E-05	Std cc/s		

Table 3: Leak test made on Rack 1



General Information				
Experiment:	CMS	Target Leak flow at reference conditions:	< 3,00E-03	STD cc/s
Sub-detector:	R134a recuperation system			
Module:	Test 2		< 0,00	l/day
Rack:	2			
Test Method:	Pressure decay method.	Pressure Measurement:		
Persons performing test:	Marco di Toma	Gauge or sensor used:	PI blondelle	
Test Location:	164	Smallest readable unit:	0,01	bar

Leak test parameter					Gas:	He
	Start		End		Difference	
Time (e.g. dd/mm/yy hh:mm):	08/02/2023 11:05		10/02/2023 16:50		193500 53,8	s h
Pressure Inside:	0,92	bar	0,92	bar	0	bar
Pressure outside:	0,983	bara	0,987	bara	-0,004	bara
Delta P:		bar		bar	0	bar
Temperature:	18	°C	18,7	°C	-0,7	°C
Volume:	9300	cm^3				

Results				
Leak at test conditions:	2,60E-05	Std cc/s	Leak rate conform to specification:	YES
Leak flow at reference conditions:	2,94E-05	Std cc/s		

Table 4: Leak Test made on Rack 2

The two tables show the same values as the two tests were conducted at the same time, therefore with the same initial conditions. Such a low leakage value does not mean that the system is leaking, but is due to the inaccuracy of the measuring instruments, such as the pressure sensor used and the temperature sensor.

Concluding the section on prototype construction and leaks, it is necessary to briefly introduce the tools used for leak detection. Sometimes leaks are clearly visible, while most of the time they can be very small, so a tool is needed to identify their location in order to repair them. The instrument used is called leak detector and its operation requires the use of helium. One of the reasons why helium is used is because in addition to being an inert gas, it is one of the 'smallest' gases present, so if critical parts do not have helium leaks, they will not have leaks of other atomically 'larger' gases. For this reason, the system is filled with pressurised helium and then the search for the leak can begin. The instrument used has an external probe, which continuously intakes and a display on which it is possible to see the ppm of helium present in the portion of gas aspirated. The higher the ppm of helium, the closer the leak will be. To detect the helium, the leak detector contains a very compact mass spectrometer inside which allows the gas to be identified.

Table 5: Helium leak detector

The mass spectrometer measures the mass-charge ratio of ionised particles by using an analytical technique. The molecule is ionised typically through electron bombardment, which can cause the molecule to break apart or simply ionise it. The fragments or ions are accelerated and placed under an electric or magnetic field. According to their mass-to-charge ratio, they are separated, and it is therefore possible to 'catalogue' them based on their deflection. An electron multiplier is responsible for their detection as it is able to detect charged particles. The intensity of the detected ions is displayed as a function of mass-to-charge ratio. Molecules are identified by comparing known masses or characteristic fragmentation patterns.[24]

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[24] de Hoffman E, Stroobant V (2001). Mass Spectrometry: Principles and Applications (2nd ed.). John Wiley and Sons.

5. Process Logic & System Electronics

One of the fundamental steps required to realise the prototype is the development of all the logical processes that determine its automatic operation. Using functional analysis, it is possible to summarise schematically all the logic behind the prototype's operation. The ensemble of pneumatically controlled valves, temperature, level and pressure sensors constitutes a large apparatus that needs to be organised in such a way that the prototype functions correctly and, furthermore, can be promptly intervened in the event of error or danger.

Functional analysis is followed by the programming phase in which everything that was schematically expressed in this phase is put into computer-readable code that will act as the prototype's actual brain. The computer or PLC - Programmable Logic Controller is the instrument that reads the input signals from the various sensors and determines the actions to be taken based on the code loaded on it. The actions are always an electrical signal that will be sent to what will be called 'actuators'. Everything is housed in a rack that physically contains the PLC, the inputs and outputs of all the analogue and digital signals, the transformers that will power the system and the Atex systems that are essential for working in environments with the presence of flammable gases. The functional analysis carried out for the R134a recovery prototype will be explained in detail below, along with a brief outline of the electronic control rack and the various components within it.

5.1. Functional Analysis

An industrial plant, as far as the process control is concerned, can be defined as a hierarchy of units. The global requirements are then organised in requirements applicable to the plant-wide control and requirements applicable to the control of a particular plant unit. This decomposition is based on the approach defined in IEC 61512-1 or ANSI/ISA S88.[25]

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[25] IEC 61512-1 or ANSI/ISA S88. Batch Control - Part 1: Models and terminology. 1995.

Terminology

Terminology is necessary for a correct explanation of the contents and is also a way of univocally defining the components and functions of the system to be described. The prototype will present the following components and functions:

Actuator: defined as control module in IEC 61512-1:

- A piece of equipment acting on the plant;
- Acts as a single entity from a control standpoint;
- Is the direct connection to the process and can embed sensors;
- Cannot execute procedural sequences;
- Examples: valves, motors, pumps, fans etc.

Unit: defined as unit and equipment module in IEC 61512-1:

- Collection of actuators and/or other units
- Can carry out a finite number of minor processing activities
- Contains all the necessary processing equipment to carry out these activities
- Can execute procedural sequences
- Examples:
  - Compression station : 3 compressors + 4 valves
  - Compressor : 1 motor + 1 valve

Controller: Regulation algorithm able to control a process variable (ex: PID controller)

Object: Unit or Actuator or Controller

Operational State: unit can be setup in different operational states (ex: Cooling, Heating).

Interlock: Asynchronous condition stopping an actuator or a unit or preventing from starting for security reasons. An interlock must not be used for normal operation but for abnormal behaviour. Software interlocks are not guarantying human security.

The possible interlocks for a complete unit or for an actuator are:

- Full stop interlock (FS): Stop the unit/actuator (all dependent units/actuators are set to their fail-safe position) and wait manual acknowledgement before restarting.
- Temporary Stop Interlock (TS): Stop the unit/actuator (all dependent units/actuators are set to their fail-safe position) and restart automatically when the interlock disappears.
- Start Interlock (SI): Prevent the unit from starting (all dependent units/actuators stay in their fail-safe position).

Alarm (AL): It is an indication of a potential problem. In this case, there is no action.

User command: Specific operator order to specify a particular action.

Computed Variables: Values computed from a set of I/O signals or from parameters.

Object numbering: In order to make immediate the understanding of the numbering of the various objects, it is necessary to introduce a legend. The name of each object will be expressed by a literal part and a numerical part.

The literal part follows the following logic:

- TE – Temperature sensor;
- PT – Pressure transmitter (digital);
- PI – Pressure Indicator (analogue);
- YV – Pneumatic valve;
- XMFC – Mass flow controller;
- FE – Flow meter;

- HV – Manual valve;
- LSH – Level sensor (liquid);
- DPT – Differential pressure transmitter (digital);
- PCV – Pressure control valve (back-pressure valve);
- FIV – Rotameter;
- WS – Weight scale.

The numerical part follows the following logic:

- 10xxx – Recuperation system;
- xx1xx – number of the column, in this case the first;
- xxx1x – Pneumatic valve;
- xxx2x – Manual valve;
- xxx3x – Pressure transmitter/indicator;
- xxx4x – Weight scale;
- xxx5x – Differential pressure transmitter;
- xxx6x – Level sensor;
- xxx7x – Temperature sensor;
- xxx8x – Mass flow meter/controller;
- xxx9x – Pressure control valve;
- xxxx1 – The number of the component in its category.

Description

The description of the system allows to summarize the complete functioning of the prototype ensuring a rapid understanding, and the schematic representation allows to summarize conceptually what has been expressed in the description, through a block flow diagram, much more intuitive and immediate understanding.

The R-134a recuperation system is a system designed to recuperate R-134a from the gas mixture of the ATLAS and CMS RPC systems. The recuperation system takes the flow coming from the output of the purifiers and separates R-134a from impurities (such as Air, N2) and from i-C4H10 and SF6, which are present in the standard RPC gas mixtures. The distillation process happens by sending the gas into one column at time. A single column is a unit composed by an input and output valves, a top “cold” chilled buffer and a bottom “warm” chilled buffer. Each column should work independently from the other columns, allowing the system to be horizontally scalable. The gas goes through the input of one column and arrives to the first top buffer. The gas mixture R-134a/i-C4H10 gets liquified, while the SF6, N2 remains in vapors form and exit from PCV-10X90. The separation of R-134a from i-C4H10 happens through a continuous change of phase between liquid and gas happening from the top buffer to the bottom one. Since the gas mixture is an azeotrope, pure cryogenic distillation is not possible, so i-C4H10 is exhausted with some R-134a vapors from PCV-10x90 as well. At the end of such resting process where the mixture continuously travel between top and bottom buffer only pure R-134a remains. At this stage, the R-134a in the column is extracted by means of a compressor, which brings the R-134a from the column to a main storage tank.

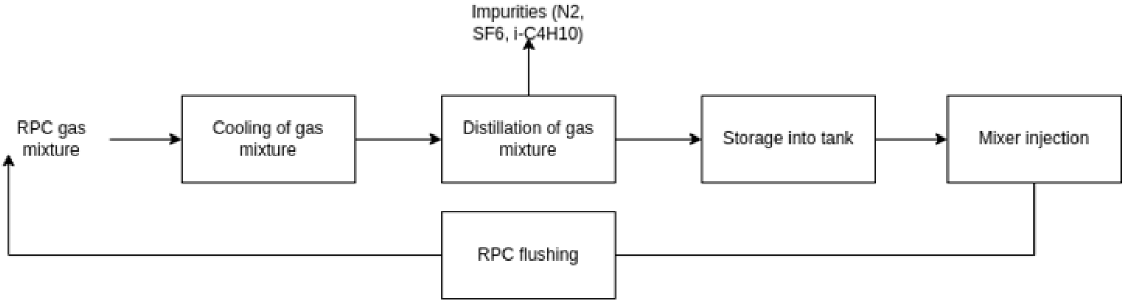

Figure 46: Block flow diagram of the process

Process decomposition

The process can be decomposed in several units which can be operated individually as defined in IEC 61512-1 or ANSI/ISA S88. The process decomposition must respect all the following constraints:

- Top to Bottom;
- Modular;
- Hierarchical;

- Structured.

To make such process decomposition in units:

a) A unit always embeds at least one other unit or one actuator.

b) Always define a “top parent unit” representing the whole plant.

c) Split the plant in independent “child units” which could be operated individually.

d) Associate eventually actuators to the top unit if they cannot be attached to other units.

e) Repeat steps ‘b’ and ‘c’ until the units contain only actuators.

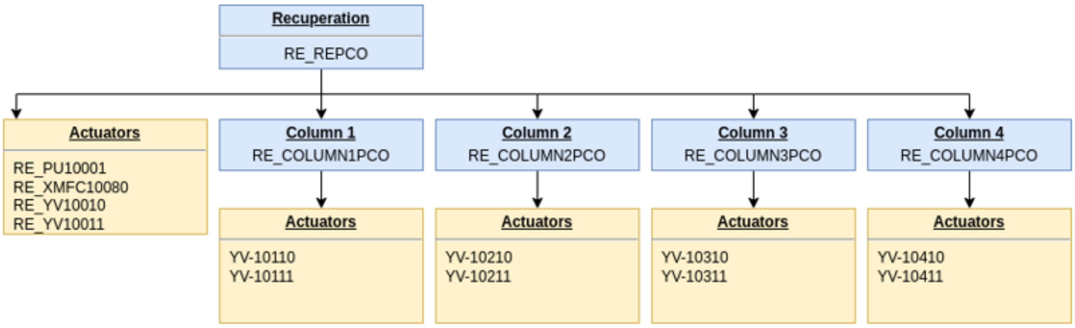

Figure 47: Process decomposition of the system

Functional analysis follows a Top Bottom approach, as expressed above, so that once described the system in general and carried out the process decomposition, it is possible to go down a level of detail to analyse the units. They are divided into two levels where the Main Unit contains the other units corresponding to the columns.

5.1.1. MAIN PCO

The main unit is defined as the recovery unit since it is the unit that manages the sub-units representing the columns. It is as if it was the column manager which according to their conditions has the function of directing the incoming flow and managing it. The recuperation unit is the main unit that controls the underlying column units. When in Run mode, the unit checks the status of the enabled columns: if there is one available column it starts the filling of the column until in full state. Once the column is full it switches to the next available column. In case no columns are available, the gas is exhausted through the exhaust by opening YV-10011 (pneumatic valve).

It is necessary to define all the components that the unit in question can handle. in this case the controlled units and the controlled actuators are taken into account.

Controlled units

- Column 1-4: The distillation columns. 2 columns physically present in each rack.

Controlled actuators

- PU10001: Recuperation compressor
- XMFC10080: Recuperation input mass flow controller
- YV-10010: Recuperation Input Valve
- YV-10011: Recuperation Exhaust Valve

OPERATIONAL STATES

Operational states are defined based on the behaviour the unit can assume. Each state in which the unit may find itself must be defined. With them also come the stages of transitions by which the unit can pass from one operational state to another.

The unit is either in stop or in run mode, depending on the Run Order request. If Column X is available and fulfilling condition 1, the system goes in run. Whereas, in

Stop mode the unit controls the safe position of all actuators and thus also of the units it controls.

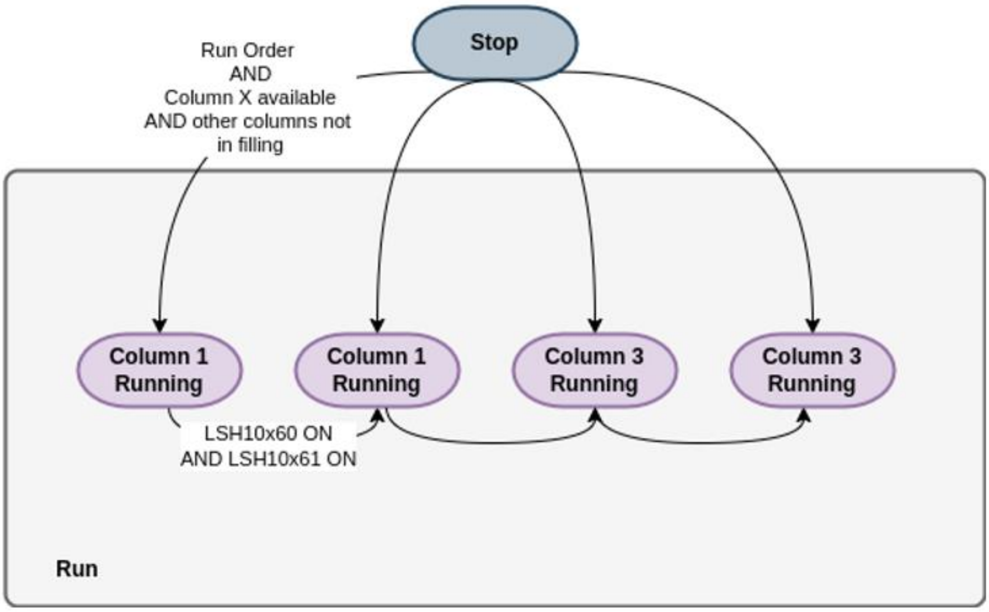

Figure 48: Process control diagram of the system

As can be seen in Figure 48, there are two operational states:

- Run: The system is running, checking if at least one column is filling and putting the first column available to fill otherwise. Checks if the filling column is full. If filling columns state = full, request the column to go in emptying state by switching on PU-10001 and request full for next available columns. If no available columns and no filling in any of the columns, open valve YV-10011 (Exhaust pneumatic valve)
- Stop: The system is stopped with all actuators in their fail-safe position.

TRANSITION CONDITION

Transition conditions, as previously expressed, are the intermediate conditions in which the unit may find itself. They therefore allow the transition between one operational state and another. Table 6 summarises the concept expressed.

Name	Condition
Stop -> Run	Run order AND *availability_condition* Any of the Column status = standby or any of the column status = stop
Run -> Stop	Stop order OR NOT *availability_condition*

Table 6: Transition conditions

The *availability condition* is the condition in which the column is in such a way that it is usable for the Run command.

LOGICAL SEQUENCES

Logical sequences express what is conceptually imparted to the unit in the form of a code. The Run state is analysed as it has multiple conditions.

During “Run” state, the unit performs the following operation:

1. Checks that there is at least one column in “Filling” mode: if true, nothing happens.
    a. If false, check if at least one column is available for filling:
        i. If True, change the state of the first column that is available for filling to “Filling”;
        ii. If False, Unit Full Stop Alarm **NoColsAvailableDA** “No columns available for filling” should be active.

Actuators behaviour

This section defines all behaviour that the actuators contained in the unit may exhibit in the operational states, which in the case of the main unit are stop and run.

	Stop	**Run**
ColumnXPCO	OFF	ON
YV-10010	ON	ON
YV-10011	ON	OFF
PU10001	OFF	ON if ColumnX.state = Extraction
XMFC10080	OFF	XMFC10080 setpoint = RecupSetPoint

Table 7: Actuator behaviour

The Table 7 resume the actuators behaviour present in the Main PCO.

PARAMETERS

This section defines the parameters, useful for process control purposes, which are accessible to the operator who can change their initial values. The parameters defined are related to the main unit.

Parameter	**Description**	**Initial value**
RecupSetPoint	Setpoint of XMFC10080	400 ln/h
FlowInjH, HH, L, LL	Injection limit alarms	
xMFC10080ConvFactor	Conversion factor to apply to R-134a MFC for standard mix	0.95
EffCalcSelection	Calculation of efficiency: 0 = use FE10082 before compressor, 1 = use tank weight, 2 = use FE10X80	
DewPointThresh H, HH	Dew point limit alarms	-40

Table 8: Parameter related to Unit recuperation.

In the Table 8 is it possible to notice the “RecupSetPoint” which is defined ad default to 400 l/h, but being a parameter it can be changed by the operator in order to test the prototype in other conditions.

COMPUTED VARIABLES

This section contains all requirements concerning dedicated calculations on variables/parameters which will then be displayed in the HMI - human-machine interface. This information is useful as it immediately provides the status of the entire system, and by automatically programming the calculations to be performed, it allows parameters such as efficiency or parameter conversions to be displayed in real time.

Name	**Type**	**Unit**	**Description**
InjFlow	Real	ln/h	XMFC1080.ActSP * InjMFCCorrFactor
TotFillVol	Real	l	∫ XMFC1080.ActSP * dt
TotExtractedVol	Real	l	∫ FE10082 * dt
CurrEfficiency	Real	%	If EffCalcSelection = 0 THEN InjFlow / MFMxx ELSIF EffCalcSelection = 1 THEN (∫ InjFlow / 22.4 * 0.102)/ WS10040 ELSIF EffCalcSelection = 2 THEN (∫ InjFlow - ∫ FE10x80) / ∫ InjFlow

TotEfficiency	Real	%	TotExtractedVol/TotFillVol * 100
AvgEfficiency	Real	%	MEAN(CurrEfficiency) from t=0 to t=AvgIntegrationTime

Table 9: Computed variables related to main unit.

Table 9 resume all the computed variables which must be displayed on the HMI. The calculation of the efficiency is the most important computed variables in order to see directly if the prototype is working well.

Unit Alarms

The alarm section is the most critical of all because by setting the correct alarm values, it is possible to intervene in the event of a fault or danger. A threshold too close to the operability threshold will always trigger the alarm unnecessarily, while one too far away may risk giving the operator too little margin to intervene.

The alarm table is available as Appendix 2.

The entire section was only related to the main unit, which internally manages the sub-units corresponding to the columns in the racks.

5.1.2. UNIT COLUMN “X”

In this section, the functional analysis of the individual units contained within the main unit will be analysed. Only the study of a generic column x will be reported, since the prototype has been designed for each column to be perfectly identical to the others. For this reason, it is sufficient to carry out the functional analysis for a generic one, always bearing in mind that the elements controlled by these units will have different "names".

The system may have multiple column units, for which in this document we refer to a generic column with the ‘X’ letter. Each column acts independently from other columns and follow a precise step sequence divided in three main phases: “filling”, where the gas is coming and filling the buffers; “distillation”, where the gas/liquid rests in the two buffers and R-134a gets separated from other components; “pumping” where the gas/liquid gets extracted from the two buffers; “standby” where the column is empty but ready to be filled.

Controlled actuators

YV-10X10: Column Input Pneumatic valve

YV-10X11: Column Output Pneumatic valve

Operational States

Column X has 6 different states, depending on internal condition of the column and the requirements of the main PCO. During standard conditions, after the STOP state, the states can be “Filling”, “Distillation”, “ExtractionReady”, “Extraction” and “Stand-by”. The main PCO handles the switch from one full column to another.

The ExtractionReady state is used to signal to the parent PCO that the column can use compressor PU-10001 to extract the gas. In Figure 10 is represented the process control diagram of the Column X Unit.

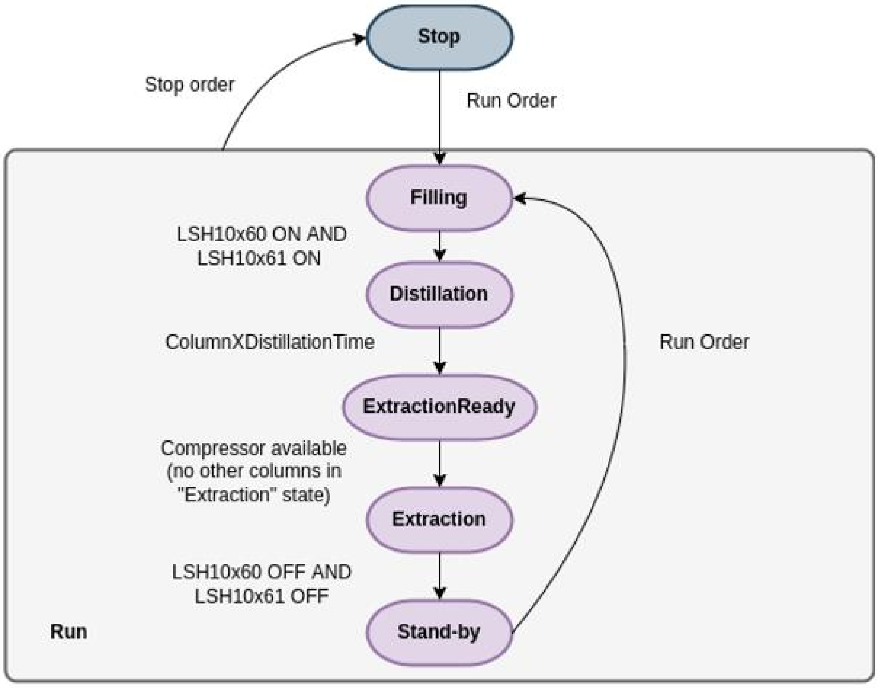

Table 10: Process control diagram of the Column X

The different operational states of column X are schematised in Table 11 below.

Step	Name	Description
1	**Stop**	The system is stopped with all actuators in their fail-safe position.
2	**Filling**	YV-10x10 is open and YV-10X11 is closed and XMFC-10080 is ON
3	**Distillation**	YV-10X10 and YV-10X11 are closed. The Timer starts.
4	**ExtractionReady**	LSH-10x61 ON and YV-10X10 is closed.
5	**Extraction**	YV-10X11 is open and PU-10001 is ON
6	**Stand-by**	Both YV-10X10 YV-10X11 are closed, both LSH-10X60, LSH-10X61 are OFF

Table 11: Operational states

TRANSITION CONDITIONS

Transition start	**end**	**Name**	**Condition**
1	2	Stop -> Filling	Run order
2	3	Filling -> Distillation	LSH-10X60 is ON and YV-10X11 is closed
3	4	Distillation-> ExtractionReady	(BuffTopFullSelection = 0 AND (LSH-10x61 is ON AND LSH-10x60 is ON)) OR (BuffTopFullSelection = 1 AND (DPT-10x50 > ColumnXFullThresh))
4	5	Extraction Ready -> Extraction	Order from Main PCO
5	6	Extraction -> Standby	LSH-10x60 is OFF AND LSH-10x61 is OFF
6	2	Standby -> Filling	Order from Main REPCO

Table 12: Transitions conditions

Table 12 summarises the transition conditions that are allowed at the level of this unit. They differ widely from the Main PCO, but are identical between columns.

Logical sequences

During “Run” state, the unit performs the following operation:

- If Column is available for filling it goes to stand-by
    - If column is not available for filling it goes to Stop
- It waits for the main REPCO to be changed in Filling status

- After filling, it waits **DistillationTime** and change its state into ExtractionReady
- It waits for the main REPCO to change its status into Extraction
- Once it's empty it goes into Stand-by

	Stop	**Filling**	**Distillation**	**Extraction Ready**	**Extraction**	**Stand-by**
Stop	/	Allowed				
Filling	Allowed	/	Allowed			
Distillation	Allowed		/	Allowed		
ExtractionReady	Allowed			/	Allowed	
Extraction	Allowed				/	Allowed
Stand-by	Allowed					/

Table 13: Logical sequences

Table 13 summarises the previously expressed concept in an easier to understand table.

Actuators behaviour

Name	Stop	Filling	Distillation	ExtractionReady	Extraction	Stand-by
YV-10X10	OFF	ON	OFF	OFF	OFF	OFF
YV-10X11	OFF	OFF	OFF	OFF	ON	OFF

Table 14: Actuator behaviour.

Parameters

The list of all parameters related to Column X is shown in Table 15. Thanks to these parameters, it is possible to modify the system's working conditions. At this level of the unit, it is possible to control pressures, temperatures and dwell times. These are the fundamental parameters that will be analysed once the tests are conducted.

Parameter	Description	Initial value
DistillationTime	Duration of distillation phase	60 mins
BuffTopFullSelection	Mode to calculate Buffer TOP full state: 0 = use LSH-10X60, 1 = use DPT-10x50	0
DPT101x50MinLevel	Minimum pressure of DPT corresponding to 0% of buffer level	10 mbar
DPT101x50MaxLevel	Maximum pressure of DPT corresponding to 100% of buffer level	40 mbar
ColumnXEnabled	Column enabled for run sequence	TRUE
ColumnXFullThresh	Threshold for column fill calculation	45 mbar
TE10x72HLim	Buffer Top Temperature H limits	To be defined

TE10x72HHLim	Buffer Top Temperature HH limits	To be defined
TE10x73HLim	Buffer Bottom Temperature H limits	To be defined
TE10x73HHLim	Buffer Bottom Temperature HH limits	To be defined
PT10x31HLim	Buffer Top pressure H limits	To be defined
PT10x31HHLim	Buffer Top pressure HH limits	To be defined
PT10x32HLim	Buffer Bottom pressure H limits	To be defined
PT10x32HHLim	Buffer Bottom pressure HH limits	To be defined

Table 15: Parameters

COMPUTED VARIABLES

As can be seen from Table 16, an efficiency calculation has also been reported for the individual columns. This is because in the event of an anomalous value in the overall efficiency, it will be possible to analyse the status of the columns by means of their separate efficiency.

Name	**Type**	**Unit**	**Description**
ColXFillVolume	Real	Liters	∫ XMFC10080 during Column filling
ColumnExtracted	Real	Liters	∫ FE10082 during Column X extraction
Column_ efficiency	Real	%	Global_Pumping_volume/Global_Filling_volume *100
ColXLiquidLevel	Real	%	Liquid_level_DPT= 0%+[(X-Xmin/Xmax-Xmin)*(100%-0%)]

Table 16: computed variables

Unit Alarms

A summary table of Column X alarms can be found in Appendix 3. As far as this unit level is concerned, it will be necessary to monitor, through the threshold values set for the alarms, pressures and temperatures of the two volumes.

5.2. PLC – Programmable Logic Controller

The term PLC stands for Programmable Logic Controller, a computer widely used in industry because of its speed and easy programming. It can be divided into 3 functions: Input, output and CPU (Central Processing Unit). First, the plc receives input signals from all the electro-mechanical components connected to it, after which they are processed by the CPU which applies to them the logic that was provided to it during programming and then later sends output signals which enable it to perform operations. The logic applied to the CPU in the form of code is nothing more than everything contained in the previous section. All the sets of definitions, logic and process patterns are translated into code readable by the PLC as well as the CPU. This is enabled by software such as Ladder Diagram, Structured Text, Function Block Diagram, Instruction List or Sequential Function Charts.

The operation of the PLC is a cyclic operation. It initially checks the status of all devices connected to the input, applies the logic provided by the programmer, and sends output signals in order to execute the states provided by the logic. It then performs a safety check so that everything works properly, and each time this step is also completed it resumes its cycle.

The PLC with all its components takes place in a rack, which is shared with the input panel. Figure 49 and Figure 50 show all the electronic components related to the PLC.

Figure 49: Back side of electrical rack

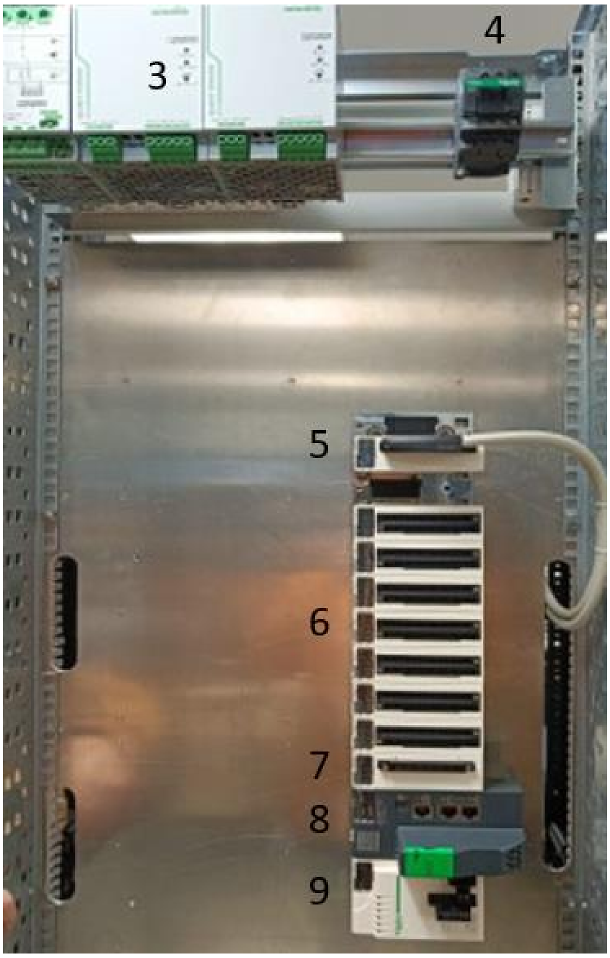

Figure 50: Front side of the electrical rack.

Legend:

1. Main power supply circuit breaker (220 V)
2. Sub-power supply circuit breakers
3. 24 V transformers and coupler
4. Emergency power circuit breaker
5. Digital Output;
6. Analog Input;
7. Digital Input;
8. CPU;
9. Bus power supply;
10. Fuses cards;
11. Atex Card;
12. Wires connections.

Electric current with 220V input first passes through the first main switch (1), and then through the sub-units switch (2). These have the function of distributing the current between the various consumers such as the system, chillers and all components that require that type of current as input. The system cannot work with that type of voltage, as the BUS, CPU and all sensors use 24 V. For this reason, two transformers (3) have been installed, which will supply the system's electrical equipment. In order to protect the circuit from possible overcurrent, fuses (10) have been installed inside the circuit which will act as a safety system.

The current that supplies the sensor and enables signal reception is all supplied by the 220 - 24 V transformers. The circuit passes from the transformers to the Digital Input (7), Analog Input (6), Digital Output (5), then through the fuse cards and finally to the sensors, closing the circuit. In the case of the R134a recovery system, working in a flammable gas environment, it is necessary to adopt Atex sensors, which involve the addition of Atex 'cards'. These components allow the power of the sensor to be modulated, ensuring that it does not ignite sparks during normal sensor operation. The circuit is also closed by passing in the return from the Atex card in order to reconvert the signal into one readable by the BUS and amperemeters.

Conclusions

The main objective of this thesis work was to recover R134a, which would normally have been released into the atmosphere, increasing greenhouse gas emissions. The subject of climate change has been fully embraced by CERN, which through several research projects is trying to find solutions in order to have the least possible impact on the environment. Numerous projects are being developed to reduce the use of greenhouse gases, as well as many others that work on recycling them. The R134a recovery prototype, designed and developed at CERN, can make a big contribution, both economically and in terms of pollution. In fact, its operating principle, based on the recovery and reuse of R134a, allows less and less of this gas to be purchased. This results in a lower emission of this greenhouse gas into the environment with a GWP of 1430.

Analysing the main phases of this thesis work, one can separate the tests conducted on the old prototype and all the construction phases of the new one. The tests were a fundamental step, as they made it possible to understand and analyse the prototype's criticalities, but above all to identify the fundamental parameters that will be the same for the new prototype once it is put into operation. During construction, on the other hand, all the criticisms that arose and all the various techniques used to find and solve them were analysed. In addition, the last fundamental aspect to be taken into account for the development of a functioning prototype is everything related to software management and electrical connections. The composition of a logic diagram that can be converted into a code, the set of alarms and threshold values, constitute a fundamental apparatus for the correct application of the prototype. Finally, as well as the assembly of the mechanical components constituting the prototype, the electrical and electronic components were analysed. They were analysed in detail, starting with the 220 V input current, passing through the signals sent by the sensors, and ending with the signals read by the PLC. Each component was specially designed and built for the development of this prototype, making it a unique, handmade prototype.

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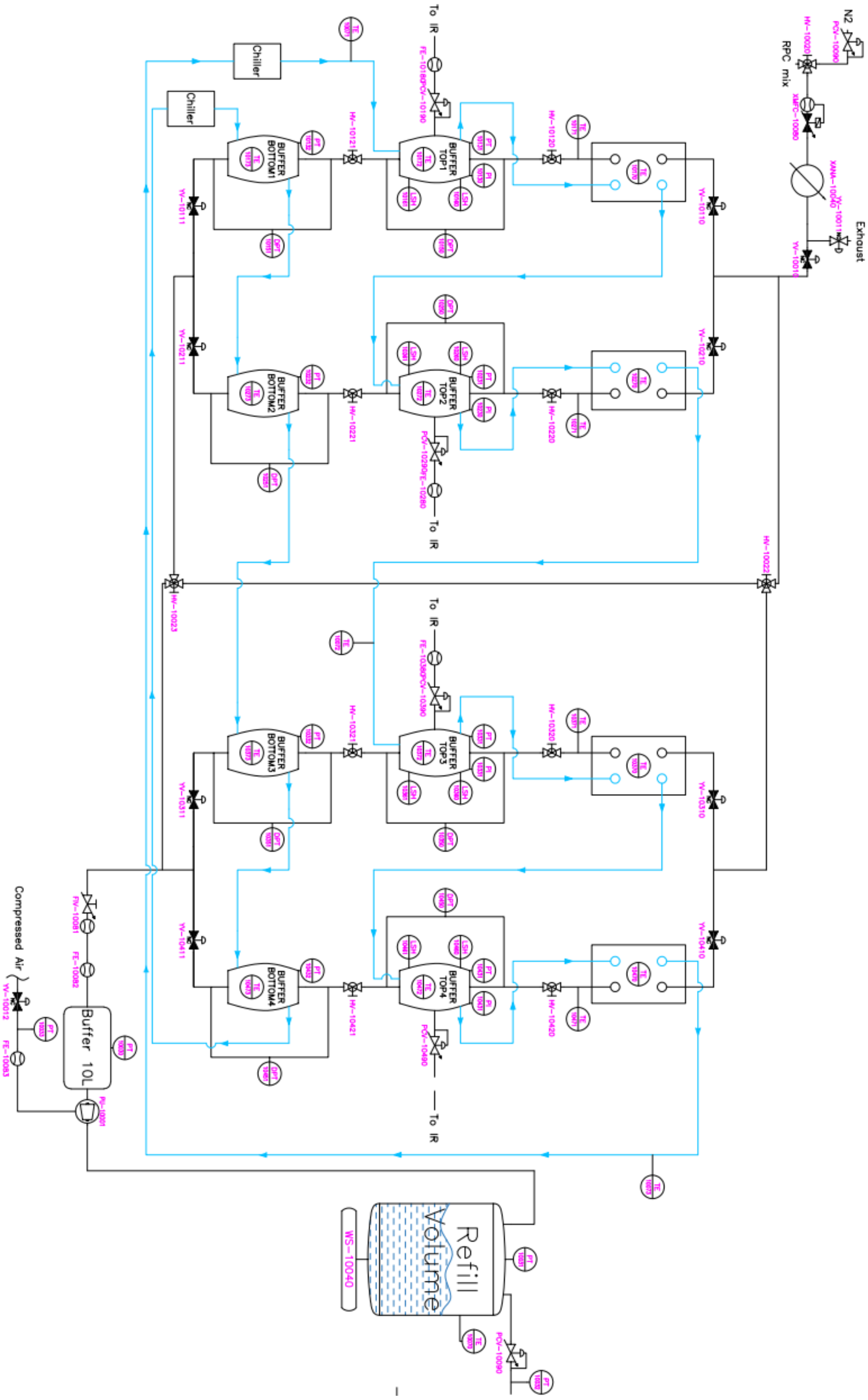
Soluzioni non ideali: deviazioni dalla legge di Raoult e azeotropi https://www.appuntimania.com/scientifiche/chimica/soluzioni-non-ideali-deviazion63.php

Appendix

Attachment 1



P&ID Prototype "II"

Attachment 2

Alarm	**Condition**	**Action ***	**Message**
NoColsAvailableDA	REPCO.x = RunOrder AND (ColumnXPCO NOT available for each Column in Columns)	FS	No Columns available for fill
FlowInjAA	FlowReg HH : FlowInjHH H : FlowInjH L : FlowInjL LL : FlowInjLL	AL	Flow Injection outside limits
CompressedAirAA	PT10033 HH : PT10033HH H : PT10033H L : PT10033L LL : PT10033LL	AL	Pressure from compressed air outside limits
DewPointAA	XANA10040AA HH : DewPointThreshHH H : DewPointThreshH	SI	Dew point gas mixture too high

Alarm	**Condition**	**Action***	**Message**
CMSRPC_Re_CoolingInputAA	CMSRPC_Re_TE10071HH HH : CMSRPC_Re_TE10071HH LL : CMSRPC_Re_TE10071LL	AL	Cooling input temperature outside limits
CMSRPC_Re_CoolingMiddleAA	CMSRPC_Re_TE10072HH HH : CMSRPC_Re_TE10072HH LL : CMSRPC_Re_TE10072LL	AL	Cooling middle temperature outside limits

Alarm	**Condition**	**Action ***	**Message**
CMSRPC_Re_CoolingOutputAA	CMSRPC_Re_TE10073HH HH : CMSRPC_Re_TE10073HH LL : CMSRPC_Re_TE10073LL	AL	Cooling output temperature outside limits

**FS = Full Stop Interlock; TS = Temporary Stop Interlock ; SI=Start Interlock ; AL=Alarm*

Unit alarms

Attachment 3

Name	**Condition**	**Action***	**Message**
CXBuffTopTempAA	CMSRPC_Re_TE10172 LL :CMSRPC_Re_TE10x72LL L :CMSRPC_Re_TE10x72L H :CMSRPC_Re_TE10x72HH HH :CMSRPC_Re_TE10x72HH	AL	Column X Buffer Top temperature outside limits
CXBuffBotTempAA	CMSRPC_Re_TE10173 LL :CMSRPC_Re_TE10x73LL L :CMSRPC_Re_TE10x73L H :CMSRPC_Re_TE10x73HH HH :CMSRPC_Re_TE10x73HH		Column 1 Buffer Bottom temperature outside limits
CXBuffTopPressAA	CMSRPC_Re_PT10131 H :CMSRPC_Re_PT10x31H HH : CMSRPC_Re_PT10x31HH		Column 1 Buffer Top pressure outside limits
CXBuffBotPressAA	CMSRPC_Re_PT10132 H :CMSRPC_Re_PT10x32H HH : CMSRPC_Re_PT10x32HH		Column 1 Buffer Bottom pressure outside limits

**FS = Full Stop Interlock; TS = Temporary Stop Interlock; SI=Start Interlock; AL=Alarm*

Unit alarms