$^{14}CO_2$ air contamination monitoring system

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INTRODUCTION

- Radiocarbon, ^{14}C ($T_{1/2}$ = 5700 (30) a), is produced naturally in the atmosphere through the $^{14}N(n,p)^{14}C$ reaction, resulting in air in a $^{14}C/C$ relative abundance of 1.2 parts per trillion (ppt).
- In a nuclear power plant, ^{14}C is produced through reactions involving thermal neutrons in the reactor core, as well as with ^{17}O and ^{13}C found in reactor coolant, moderator, and fuel, with a $^{14}C/C$ relative abundance within the range of 1 parts per billion (ppb) ÷ 1000 ppb. In its gaseous form, the produced ^{14}C is mostly bound to CO_2 and methane.
- Continuous monitoring of radioactive $^{14}CO_2$ is essential for the operation of a nuclear power plant, the operation of D&D, and the safe storage of nuclear waste materials.
- The very low levels of concentration of ^{14}C in CO_2 make the direct detection of radiocarbon very difficult.
- A new prototype for CO_2 separation and concentration system has been developed at ENEA in partnership with the Italian company Air Liquide Italia Service, as part of the CLEANDEM project funded under Horizon 2020. The system allows, by means a cryogenic method, for the separation of gas components based on their physical phase transition properties.

METHODS AND MATERIALS

(1) The SKID

- The cryogenic system, named SKID (Fig. 1), for $^{14}CO_2$ trapping (Fig. 2) was designed as a transportable station, to be positioned outside the inspection area in a fixed position and to be able to be connected to an Unmanned Ground Vehicle (UGV) robot, designed and built in the CLEANDEM project, used for inspections in a nuclear site and /or radioactive waste laboratory.
- The SKID is able for producing about 1/2 mole of CO_2 (23 g roughly) in a cycle of about 4 hours. It is equipped with a dewar of 180 L of nitrogen liquid (in Fig. 1 outside the cabin where the SKID is installed) which is used to freeze and capture the CO_2

Figure 1. *The SKID with the 180 L dewar of liquid nitrogen*

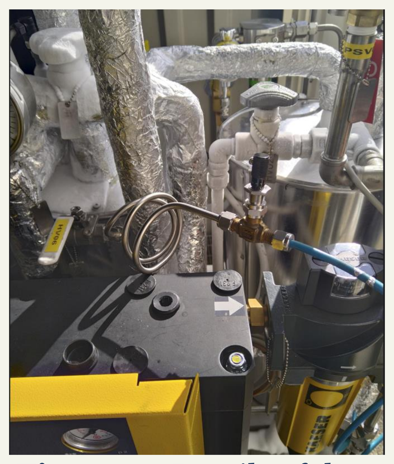


Figure 2. *Details of the cryogenic $^{14}CO_2$ trapping*

(2) The SKID design

- The SKID design is shown in Fig. 3
- The air to be processed is sucked via a hose (length 10 m; DN =20/25) **(1)** which represents the mobile instrument of collection of the analysis sample, and the link between the UGV and the SKID.
- The air is then sent to a vane compressor **(2)** working at a pressure until 6 barg to dry it in **(3)**
- **E01** and **E02** are the two heat exchangers (**HE**) for CO_2 solidification.
- **E01** cools the incoming air flow to around -140° C by utilizing liquid nitrogen at around -180 °C. **E01** freezes and solidify the captured CO_2 to -140°C through continuous interaction with the external 180 L liquid nitrogen dewar. **E02** is an enthalpic heat recuperator by cooling incoming air with exhaust air from **E01**. When the cycle ends, in the **E01 HE** the solid CO_2 produced is returned, by heating, to the gaseous phase and made available to the user.

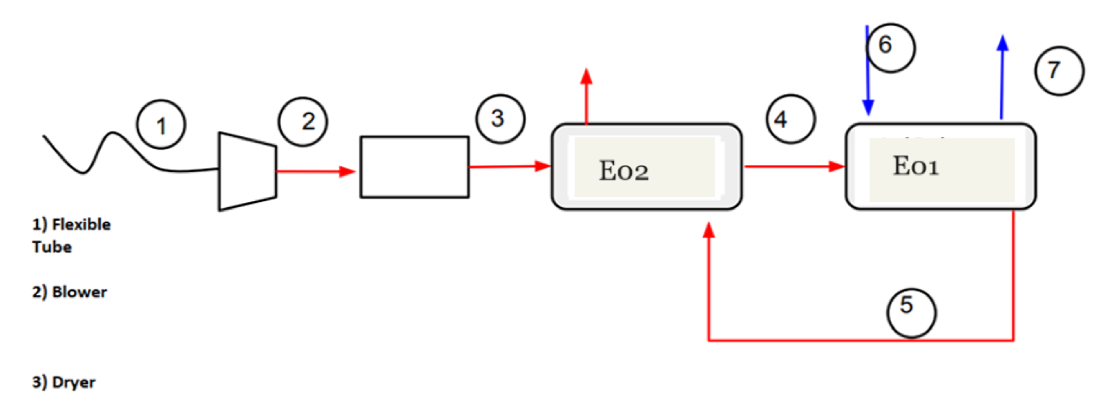


Figure 3. *The SKID design*

(3) Samples preparation for Liquid Scintillation Counting (LSC)

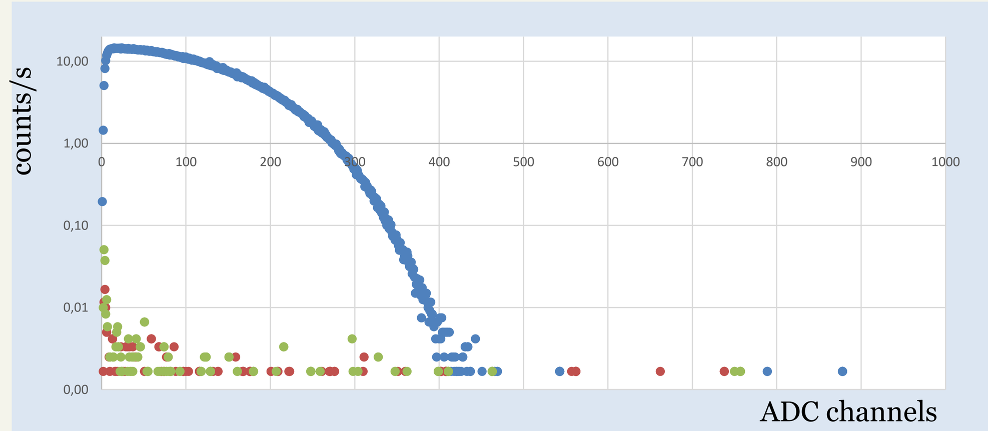
- To perform an initial assessment of the radiocarbon (^{14}C) levels in the CO_2 generated by the SKID, a 20 ml *Carbo-Sorb® E* liquid solution was used to capture carbon from pure gaseous CO_2 using adequate instruments, including a bubbler, to spill the gaseous CO2 from the SKID (Fig. 4-a and Fig. 4-b).
- From the above liquid solution, two samples (radiocarbon samples) were generated in 20 ml high-performance (low potassium content) glass vials, each one containing 10 ml of liquid scintillator Ultima Gold (UG) and some aliquots of the *Carbo-Sorb® E* liquid solution
- Additionally, two other samples, one containing approximately 2 kBq of pure ^{14}C and the other one only 10 ml of UG liquid scintillator (blank sample), were prepared under the same conditions as the previous ones.

Figure 4-a. *Set of instruments to spill the gaseous CO_2 by the SKID*

Figure 4-b. *CO_2 bubbler to capture carbon through gas flow over CARBO-SORB E*

RESULTS

- The four prepared samples were measured for 5 repetitions, each lasting 20 minutes, in the Liquid Scintillation Counter (LSC) system TRICARB 3100TR available at the Radioactivity Laboratory of ENEA-INMRI.
- The LSC system works with a ^{3}H efficiency of 61.4% and a ^{14}C efficiency of 92.2%.
- The spectra of all measurements carried out with the TRICARB 3100TR LSC system were recorded, along with the raw data including the start of measurement, time of measurement, and counts recorded across the entire available channel range.
- The net count rate of the ^{14}C-standard source (blue points) and radiocarbon sources (other coloured points) are shown in Graphic 1 as function of the ADC channels. From this graphic it is evident that a signal from radiocarbon samples emerges above the background in the energy region of ^{14}C beta emissions.
- The value of the net integral counting rate recorded by the TRICARB 3100TR LSC system for radiocarbon samples was approximately: (0.20 ± 0.02) counts/s (cps). The detection limit, L_D, estimated by the Currie law, was 0.08 cps.



Graphic 1. *Spectrum (counts/s vs ADC channels) of the measured LSC samples in the TRICARB counter for ^{14}C-standard source (blue points) and radiocarbon sources (other coloured points)*

CONCLUSIONS

1. A new cryogenic CO2 trapping system, named SKID, was built at ENEA in the framework of the funded CLEANDEM project.
2. The radiocarbon content of the pure CO2 produced by the SKID was initially assessed using the LSC technique of measurements.
3. Further researches are necessary because of the very low natural concentration (1.2 ppt) of $^{14}C/C$ in atmospheric CO_2

REFERENCES

1. L. Quintieri, P. De Felice. Development and testing of a cryogenic system for radioactive $^{14}CO_2$ gas separation for nuclear waste monitoring. Progress in Nuclear Energy. 2019 Apr 1;112:202–8.
2. CLEANDEM project: https://cordis.europa.eu/project/id/945335

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