CHANCE

Characterization of Conditioned Nuclear Waste for its Safe Disposal in Europe

CHANCE project

(Contract Number : 755371)

Report on the validation of CRDS for radiocarbon detection performances with liquid scintillation counting techniques

DELIVERABLE (D5.5)

Work Package 5

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1. Objectives and Introduction

The CHANCE project aims to address the specific issue of the characterization of conditioned radioactive waste. The characterization of fully or partly conditioned radioactive waste is a specific issue because unlike for raw waste, its characterization is more complex and therefore requires more advanced non-destructive techniques and methodologies.

The first objective of the CHANCE project is to establish at the European level a comprehensive understanding of current conditioned radioactive waste characterization and quality control schemes across the variety of different national radioactive waste management programmes, based on inputs from end-users members such as Waste Management Organizations and storage operators.

The second objective of CHANCE is to further develop, test and validate techniques already identified that will improve the characterization of conditioned radioactive waste, namely those that cannot easily be dealt with using conventional methods. Specifically, the work on conditioned radioactive waste characterization technology will focus on:

- Calorimetry as an innovative non-destructive technique to reduce uncertainties on the inventory of radionuclides;
- Muon Tomography to address the specific issue of non-destructive control of the content of large volume nuclear waste;
- Cavity Ring-Down Spectroscopy (CRDS) as an innovative technique to characterize outgassing of radioactive waste.

The present report focuses on activities from Work Package 5 related to the development of the CRDS for the detection of radioactive gases. One aim of WP5 was to validate the use of the CRDS technique for radiocarbon detection and compare its performances with more conventional techniques, such as liquid scintillation counting (LSC). The focus of this deliverable is to highlight the advantages and / or disadvantages of CRDS relative to other techniques in particular in terms of limits of detection, sensibility, etc.

^{14}C is one of the radionuclides for the performance and safety assessment of radioactive waste repository, due to its high activity concentration in some kinds of waste materials from a nuclear cycle and to its mobility. The measurement of ^{14}C content in outgassing from nuclear wastes is important for the safety assessment of the disposal and for the choice of the appropriate treatment/disposal method. This radionuclide is thus the focus of task 5.2 of CHANCE.

The detection principles of CRDS and LSC are fundamentally different. CRDS is a laser spectroscopy method, probing the molecular absorption levels, $^{14}CO_2$ in case of radiocarbon detection. It is most sensitivity when the sample is in gaseous form and is thus ideal for outgassing monitoring. LSC on the other hand, relies on counting photons resulting from the interaction of beta-particle generate by radiocarbon with a liquid scintillator (e.g. zinc sulfide). A gaseous sample therefore needs to be first bound in a liquid medium to enable a measurement.

The initial planning was to measure the same sample with different techniques in order to evaluate performances and to compare results. However, because of the pandemic it became difficult to organise and manage exchange of samples between VTT and ENEA. Measurements were carried out in VTT by using CRDS and LSC for graphite samples that allowed comparison of these two techniques. Unfortunately, it was not possible to analyse the same graphite samples by using the procedure/methods developed at the ENEA laboratory. The procedures for detection of 14C by LSC developed at ENEA are described in this report. Comparison and evaluation of application of LSC and CRDS for detection of 14C are discussed based on the results acquired in the project and on the application of these techniques worldwide.

2. Methods

Liquid Scintillation counting (LSC) and the Cavity ring Down Spectroscopy (CRDS) measurements have both their benefits for radiocarbon measurements, but also limitations. To reach the best measurement performance, the most suitable technique should be selected depending on measurement circumstances and requirements. Due to two different measurement principles Liquid Scintillation counting (LSC) and Cavity Ring-Down Spectroscopy (CRDS) analyze two different molecules containing the original carbon: benzene and carbon dioxide respectively.

As ^{14}C is a weak β-emitter, it must be isolated from all the other radionuclides in LSC, when it needs to be analysed in materials from nuclear processes. This is one of the main challenges if the carbon is within a complex matrix. This is not needed in CRDS, as absorption due to other radionuclides will occur at other wavelengths and will not interfere with the measurement of radiocarbon.

2.1 Radiocarbon detection with Liquid Scintillation Counting at the ENEA laboratory

Methods providing information on the chemical form of ^{14}C in different process media of nuclear reactors are generally based on measuring the total and inorganic ^{14}C in separate subsamples, whereby the organic fraction is estimated by subtraction (i.e., indirect measurement). This procedure led to some intrinsic uncertainties. In order to perform direct measurements of both fractions the analytical methodology should consider the chemical-physical separation of different forms.

The first step for measurement of total ^{14}C is to efficiently extract the carbon content from the samples. This step is usually done by oxidative combustion, heating the sample in air or oxygen atmosphere, and obtaining carbon monoxide (CO) and carbon dioxide (CO_2) as by-products.

$$^{12,13,14}C\text{-X (sample)} + O_2(g) \rightarrow {}^{12,13,14}CO_2 + {}^{12,13,14}CO$$

Where $^{12,13,14}C$ means that all the carbon isotopes are involved in the chemical reaction and they will maintain, as a first approximation, their constant ratio also in the by-products of the combustion. Usually, a catalytic furnace is used to ensure complete oxidation to CO_2. Figure 1 illustrates a dispositive used for transformation of the sample in CO_2.

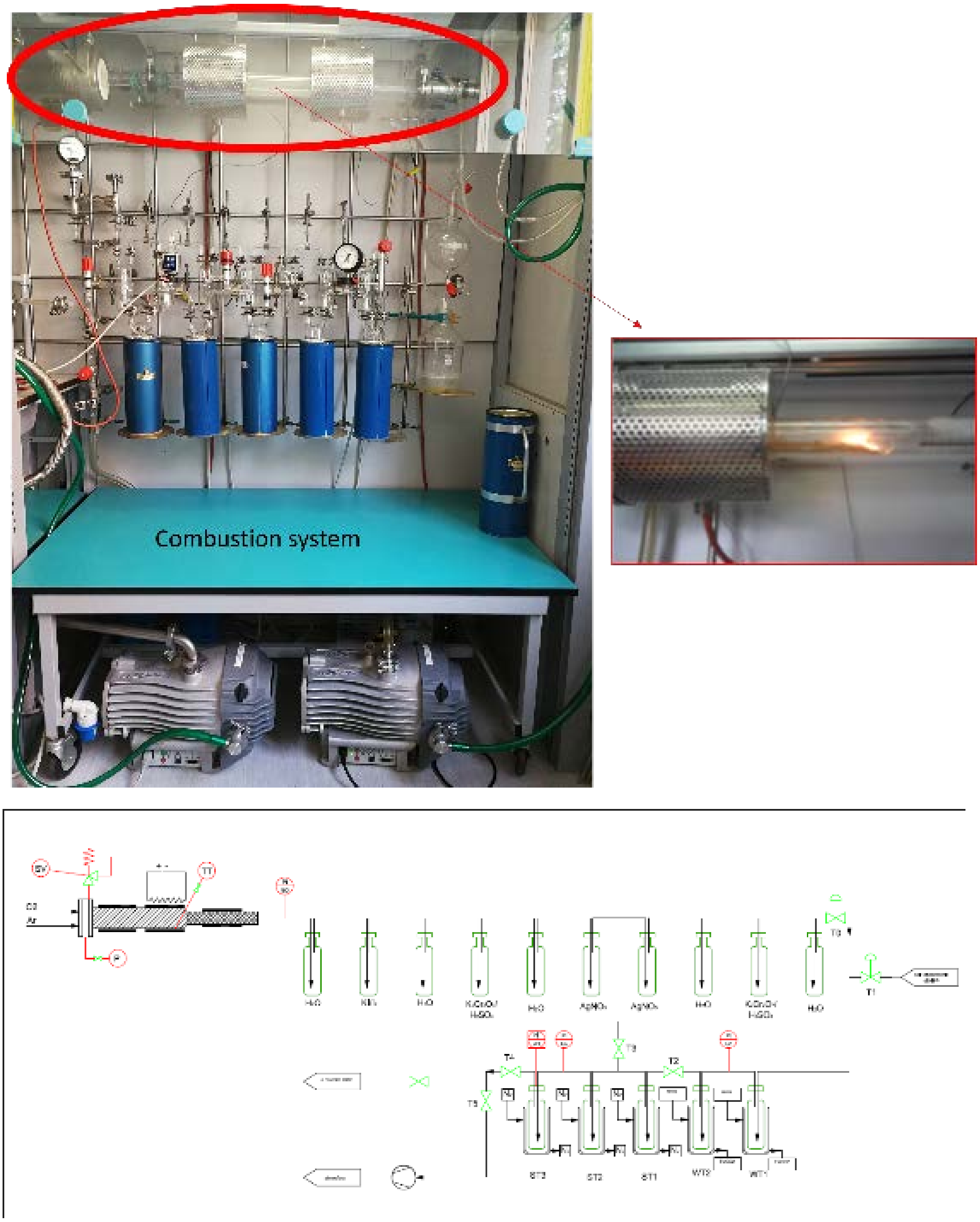


Figure 1. Schematic representation and photo of a typical combustion chamber for CO_2 transformation of the sample – photo courtesy provided by ENEA ^{14}C laboratory.

As the main purpose in this step is to extract the carbon content form the samples, the following step will be the trapping of the CO_2 in a suitable form for measuring the beta radioactivity, due to the ^{14}C. This purpose can be achieved by three main techniques that have in common the necessity to obtain CO_2 gas from the sample:

1. Accelerator Mass Spectrometry (AMS);
2. Benzene-LSC (Liquid Scintillation Counting);
3. CO_2 cocktail-LSC.

The three methods differentiate from their detection limit that increases from AMS to CO_2 cocktail-LSC technique. AMS and benzene-LSC are well-known and successful methods used by many laboratories worldwide. When the ^{14}C content is relatively high – as in biological and nuclear materials –, the liquid scintillation counting technique has been used to determine the ^{14}C concentrations[1]. Until recently, almost all quantitation of ^{14}C content was made by scintillation detection of the low energy β particle emitted in its decay, a low efficiency method as only 1 beta particle is emitted per minute for every 5 billion ^{14}C atoms present. This the why the sample itself it is chemically transformed in a scintillating molecule, the benzene, to enhance the probability to detect the beta particle emission. There are different LSC techniques for ^{14}C measurement: first of all, the carbon content of the sample is transformed in CO_2 gas and then it is either trapped in adsorption media such as alkaline solutions (NaOH/KOH) or amines and converted respectively in carbonate $CaCO_3$ or carbamate R-NH(CO)O-R', or directly converted in benzene C_6H_6 by a catalysed chemical reaction.

In alkaline solution (NaOH/KOH), the efficiency curve can be realized and calculated with a ^{14}C standard solution and established as a function of a quench index parameter (SQPE). The quenching curve is established by adding increasing amounts of acetone quenching agent to seven vials containing the same activity of the ^{14}C standard.

The ENEA ^{14}C Laboratory developed the Benzene-LSC and the CO_2 cocktail-LSC.

2.1.1 Benzene-LSC

The conversion into benzene is the most advanced techniques in LSC determination as the sample itself is transformed in a scintillation molecule, the benzene, which contains over 90 % (w/w) of carbon atoms [1]. The sample to be measured is burned in a furnace in oxidizing conditions and, after drying, the CO_2 is transformed into Lithium carbide Li_2C_2 by a chemical reaction with molten lithium metal, at 600 °C.

$$2\,{}^{12}CO_2 + 4Li \rightarrow Li_2C_2 + 4Li_2O$$

The lithium carbide is then decomposed by the addition of water and transformed into acetylene C_2H_2.

$$Li_2C_2 + 2H_2O \rightarrow C_2H_2 + 2LiOH$$

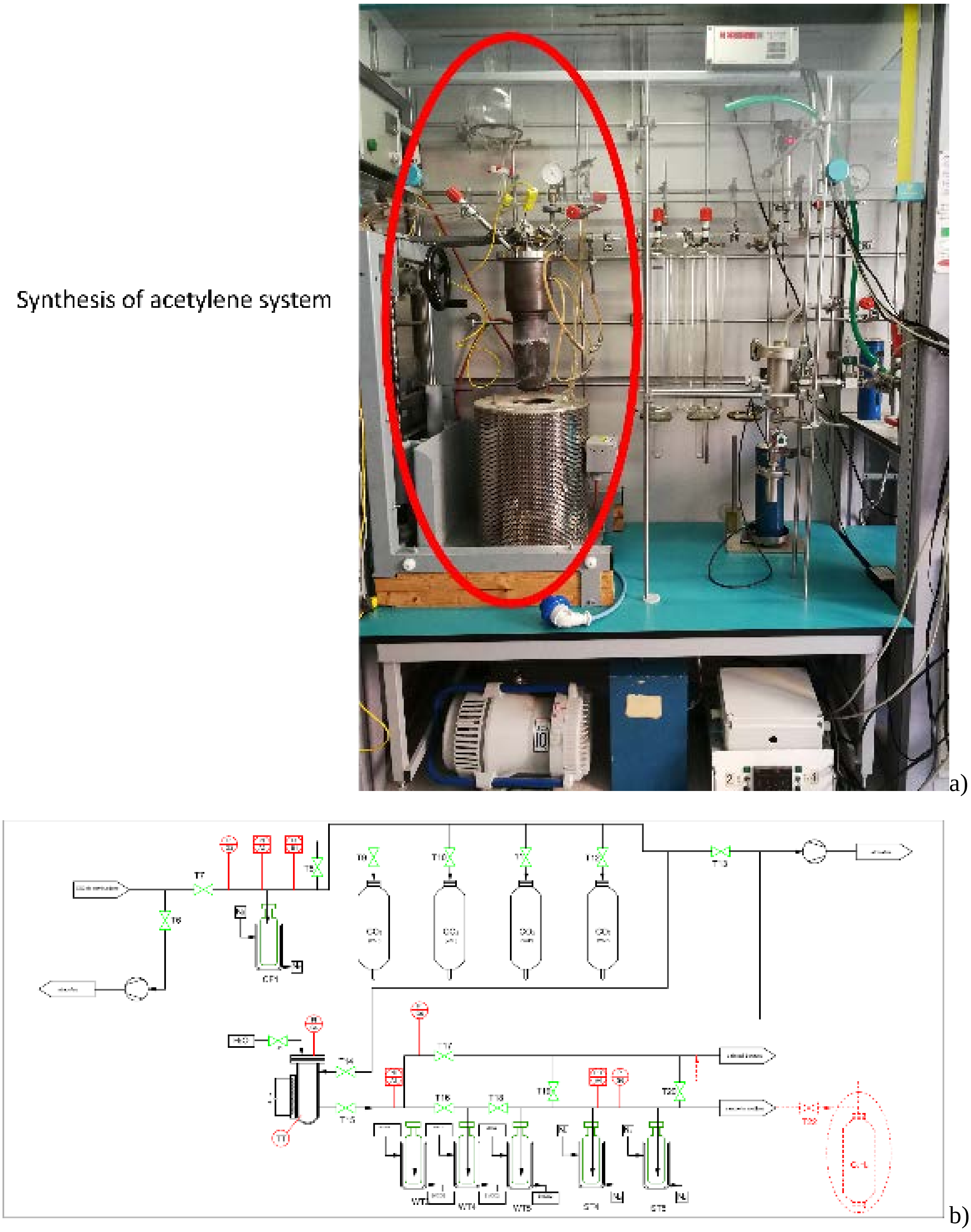


Figure 2. The synthesis of acetylene system at ENEA ^{14}C laboratory: a) photo imaging; b) schematic representation.

Finally, the acetylene is transformed in a catalysis tube (filled by trimerization catalyst beads containing Vanadium) into benzene C_6H_6 at 90 °C.

$$3C_2H_2 \rightarrow C_6H_6$$

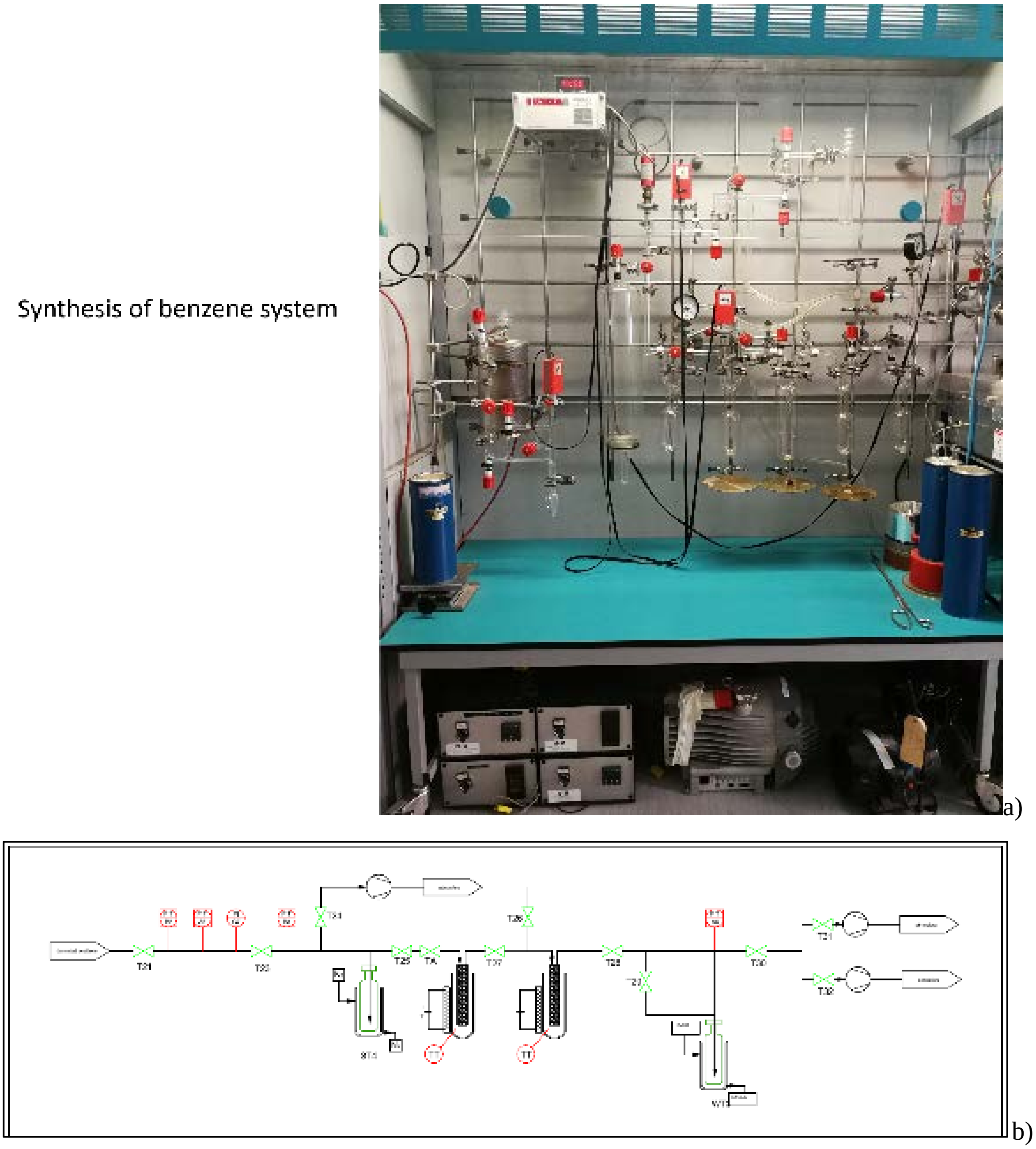


Figure 3. The synthesis of benzene system at ENEA ^{14}C laboratory: a) photo imaging; b) schematic representation.

The synthesis of acetylene system at ENEA is presented in Figure 2, while the synthesis into benzene is shown in Figure 3.

The benzene sample is then extracted and purified by condensation at 0°C and transferred in counting vial. It is then mixed with scintillation cocktail, consisting in a solvent and a scintillator, which is an organic liquid that fluoresce when energized. The vial containing the benzene sample is stored for a few hours before counting in order to avoid chemi-luminescence effects that could interfere with ^{14}C spectrum especially at the lowest energies.

The measure of ^{14}C content is made by LSC equipment that analyses the β radiation emitted by ^{14}C. The beta-particle from the sample will generate numerous of scintillator photons which can be detected by photomultiplier tubes (PMT), where an electrical pulse is generated (Figure 4). The number of generated pulses corresponds to the number of disintegrations, i.e., the activity of the measured sample.

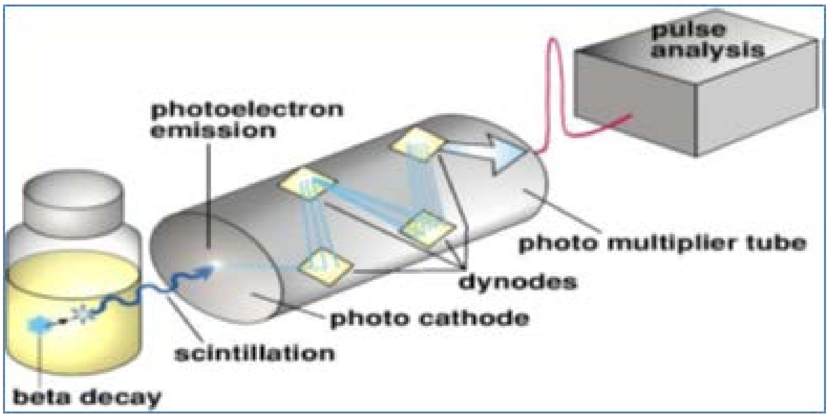


Figure 4. The β decay energy conversion and transmission mechanism to produce photons and pulse signal.

In the ENEA laboratory the most advanced LSC instruments is available in which a double shielding system is implemented in order to lower the background signals and the false positive spikes.

In Figure 5 a typical detection system is represented: one for the coincidence counting and the other one in anti-coincidence mode from the first one. The use of two photomultiplier tubes and the coincidence circuit allows lowering the instrumental background down to 30 counts.min^{-1}. An active shielding is provided by a liquid scintillator surrounding the two sample PMTs; the other two PTMs being placed outside the active shielding but inside the passive one, made by an asymmetric shield of lead. An example of a recorded spectrum with this arrangement is shown in Figure 6. The technique with benzene is very accurate but requires a great expenditure of time and costs.

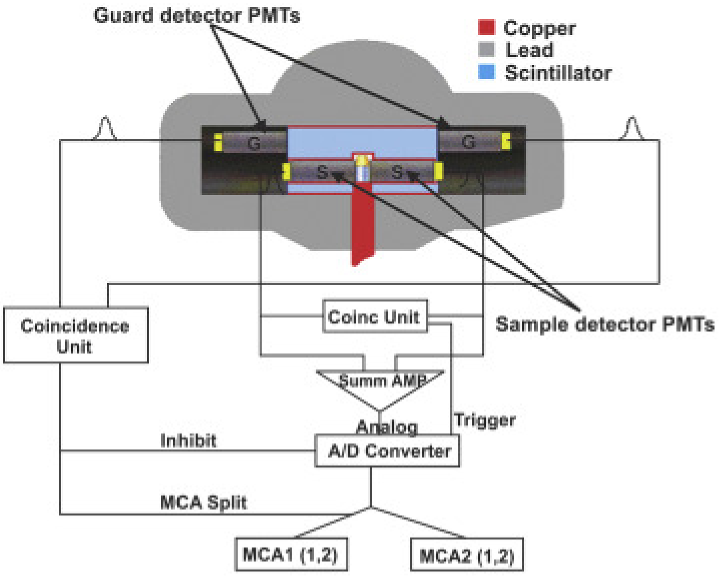


Figure 5. Internal shielding (active and passive) in a commercial LSC instrument[2].

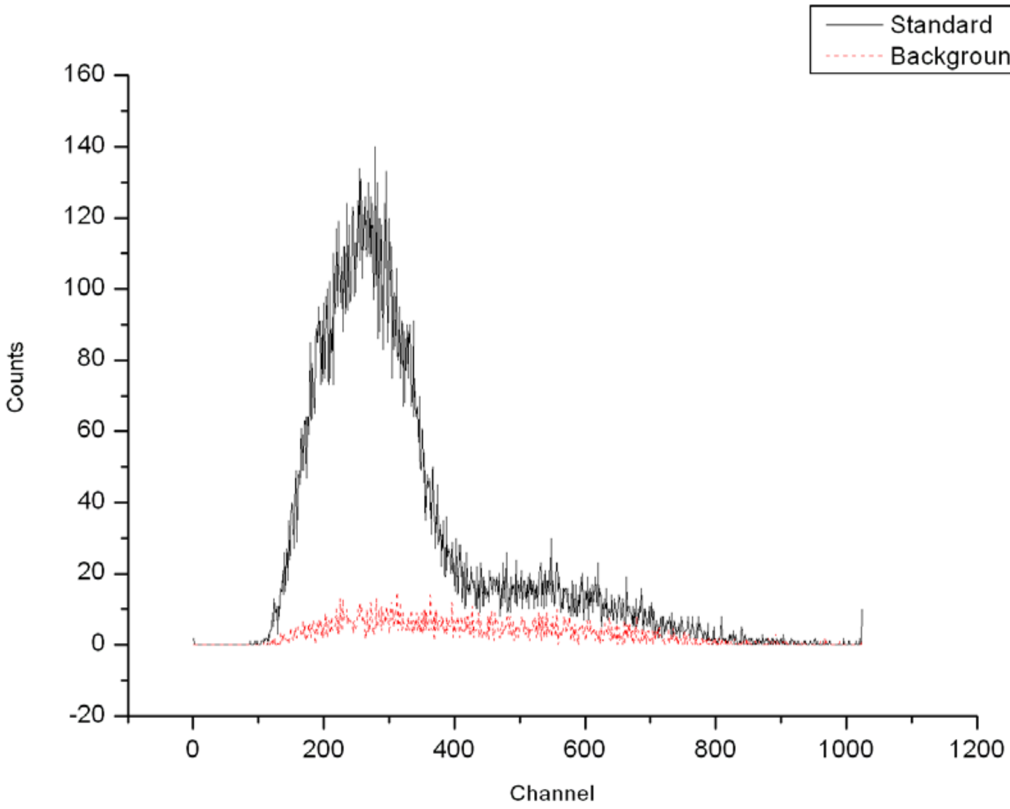
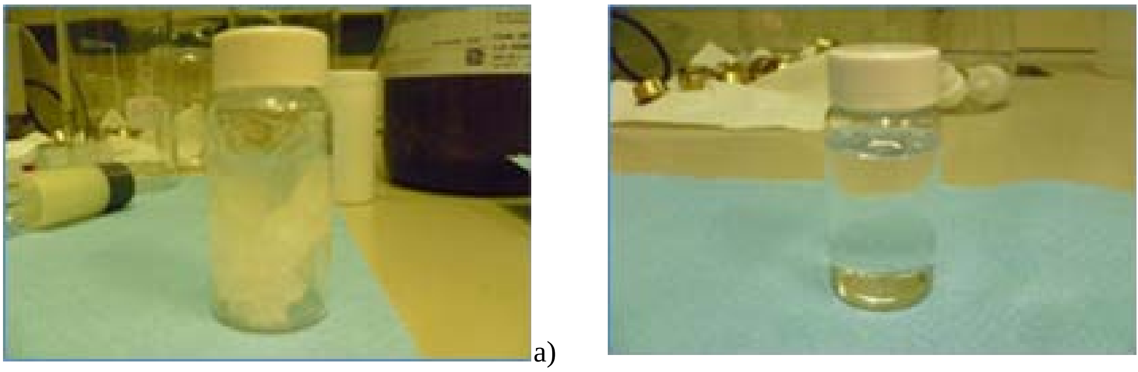


Figure 6. Typical 14C spectrum obtained by standard (black curve) and background sample (red curve) [2].

2.1.2 CO_2 cocktail-LSC

The other approach is based on the same basic principle of benzene-LSC method[3]. The main difference is that once CO_2 is produced from the sample, it is directly absorbed by a chemical/physical adsorption in specific liquid solutions. This method applies when there a is relevant quantity of ^{14}C, very similar to the one contained in atmosphere. The simpler, but least accurate method is to precipitate the carbonate by fluxing CO_2 in an alkaline (NaOH/KOH trap) and adding calcium chloride $CaCl_2$. The carbonate is then filtered, dried (to be weighted for the determination of the yield) and added by a scintillation cocktail for the LSC measurement. The most important adverse problem with this technique is the self-absorption (physical quenching) and the inhomogeneity of the suspension that could affect the counting efficiency.

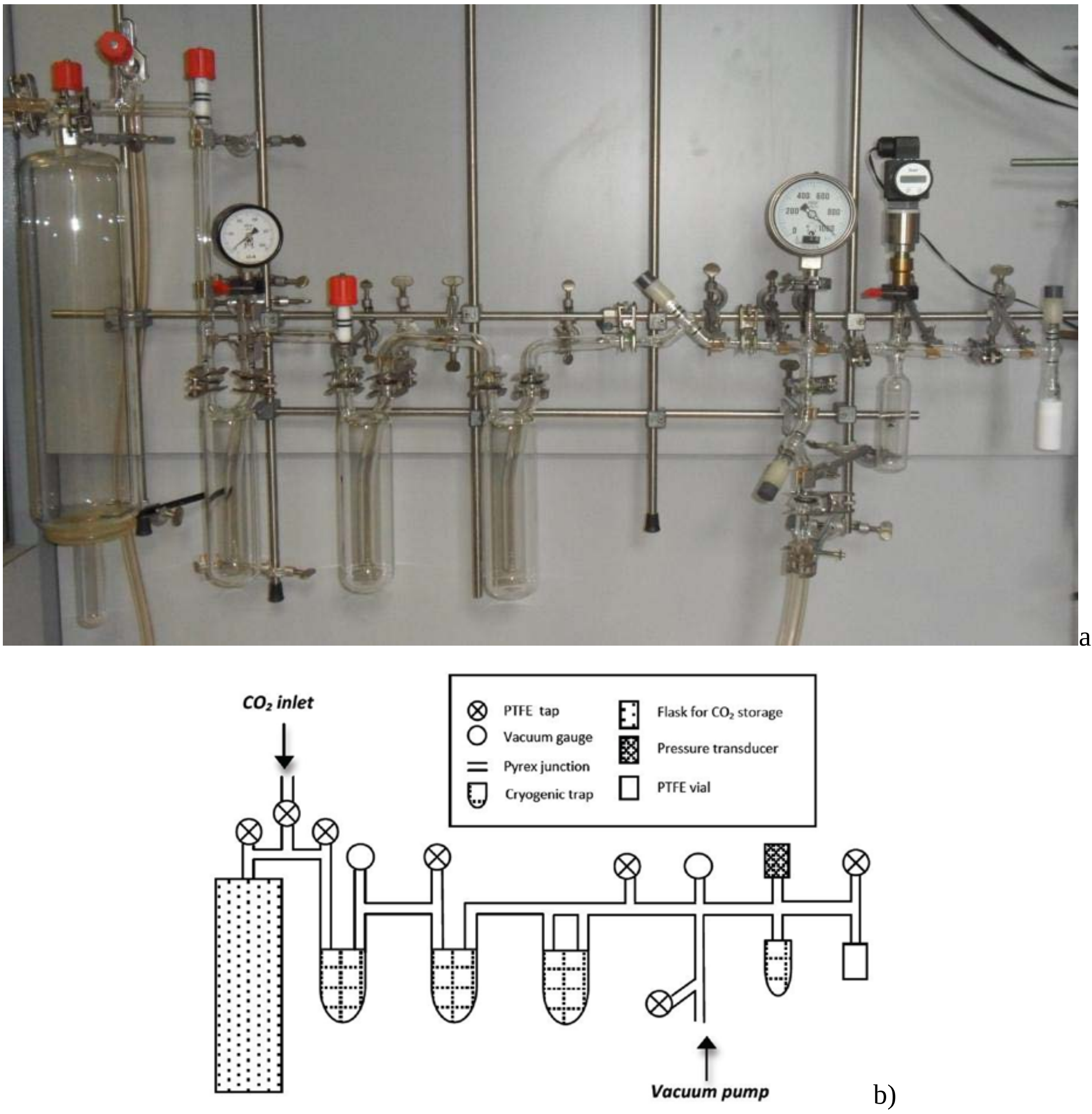
A more advanced method uses the CO_2-absorbing properties of a class of molecules such as the functionalized amines. This method is presented in Figure 7 while the CO_2 direct absorption method from ENEA is shown in Figure 8. Carbon dioxide is chemically trapped as a carbamate in a suitable absorbing solution, i.e., 3-methoxy-propyl-amine, added of methanol – in order to avoid phase separation and occurrence of high viscosity colloidal suspension – and scintillator and then analysed by LSC to determine the content of ^{14}C. Studies on the efficiency comparison of the two methods are reported in Ref [4].



a)

b)

Figure 7. Vial containing: a) formation of gel colloidal during the adsorption of CO_2 in amine without the addition of methanol; b) carbamate solution ready to be counted by LSC.



a)

b)

Figure 8. The CO_2 direct absorption method at ENEA ^{14}C laboratory: a) photo imaging; b) schematic representation.

2.2 Radiocarbon detection with cavity ring-down spectroscope

Cavity Ringdown Spectroscopy has become a widely used technique in the optical absorption analysis of atoms, molecules, and optical components. The technique allows the determination of total optical losses within a closed cavity comprised of two or more mirrors and can be made more sensitive by improvements in the cavity mirror reflectivity. Part of the great attraction that Cavity Ringdown Spectroscopy has, in addition to its great sensitivity, is the simplicity of its use.

Cavity ring-down spectroscopy (CRDS) is an established technique for trace gas detection. This approach measures changes in the rate of decay of the light injected into an optical resonator and relates the change to optical loss along the length of the resonator. In CRDS a laser that illuminates a narrow optical cavity which consists of two highly reflective mirrors. When the laser inside the cavity is in resonance, constructive interference is generated which increases the intensity of the signal. The laser is turned off to allow the measurement of the exponential decay of the light intensity. During this decay the ray of light is reflected by the two mirrors of the cavity for hundreds of times generating an optical path for the extinction of the effective length of a few kilometres. If something that absorbs light is placed in the cavity, the amount of light decreases more quickly creating fewer oscillations before running out completely. Figures 9a and 9b summarize the principle of CRDS.

CRDS measures how long the light decays to 1/e of its initial intensity, i.e., the "ring down time". Variation of the ring-down time as function of wavelength are recorded to compute the absorption spectrum (Figure 10). The wavenumber dependent absorption coefficient at the measured wavelength can be calculated using the following equation: $\alpha(\nu) = 1/[c\tau(\nu)] - 1/[c\tau_0]$, where ν is the wavenumber and c is the speed of light. τ is the decay time of the exponential decay, known as the ring-down time, measured with sample in the cavity and τ_0 is the ring-down time in an empty cavity. The mole fraction of gaseous samples that absorb light at a specific wavelength down to concentrations below parts per trillion (ppt) can then be determined. CRDS can be used to measure both highly absorbent but trace species and abundant but weakly absorbent species.

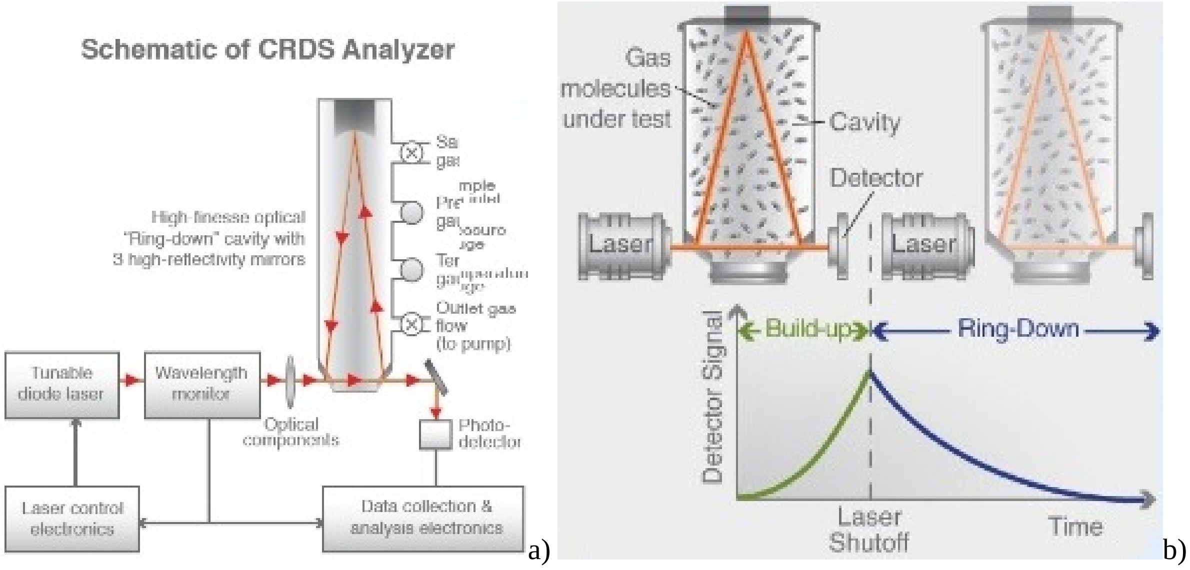


Figure 9. Functioning of the CRDS : a) schematic approach ; b) detail of the ring down time.

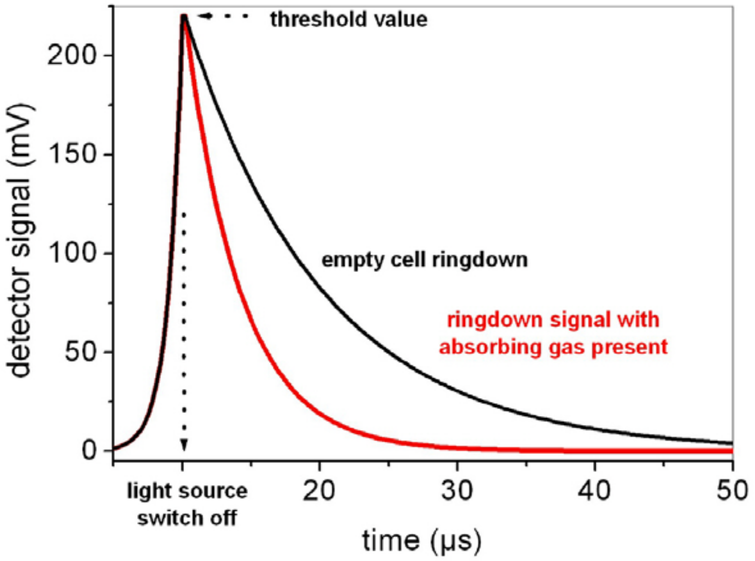


Figure 10. Ring signal with absorbing gas present in a CRDS system.

2.3 Radiocarbon detection with cavity ring-down spectroscope at VTT

The detection of radiocarbon (^{14}C) outgassing is based on the detection of $^{14}CO_2$ molecule P(20) absorption line at mid-infrared at 2209.109 cm^{-1}. The low absorption of the line because of low concentration of the $^{14}CO_2$ in the samples required using cavity ring-down spectroscopy to measure the concentration.

VTT has developed a cavity ring-down setup for C14 detection which is shown schematically in **Error! Reference source not found.**1, and further details can be found in Ref [5]. In the setup, a L12004-2209H-C quantum cascade laser (QCL) from Hamamatsu with a central wavelength at 4.527 µm was used. The laser is guided through collimating lens, two optical isolators and two mode-matching mirrors to an optical cavity formed by two high-reflectivity ZnSe mirrors. The high-reflectivity mirrors have reflectivity of 99.97 % and 1 metre radius of curvature. The second mirror is mounted on a piezo-electric actuator-controlled platform. The cavity and the mirrors are enclosed inside an insulated and temperature-controlled cell, which has antireflective-coated CaF_2 windows for the laser entrance and exit. The low pressure required by the measurements is achieved with a scroll pump and the pressure is monitored with capacitance manometer. After the second mirror the light is guided to a photovoltaic detector and the detector signal is recorded by a FPGA card. The signal is processed and analysed with a LabVIEW-based software. By simultaneously scanning the cavity length with the mirror on the piezo mount, and scanning the laser wavelength, an absorption spectrum of the scanned laser range is formed. The spectroscope is positioned to a moveable 19-inch instrument rack.

The concentration of the radiocarbon was determined by fitting a sum of Voigt profiles with a non-linear least-square fitting routine to the measured absorption spectra, which were first smoothed with a moving-average filter. To obtain the radiocarbon concentration, the total CO_2 concentration in the cavity needed to be measured. This was done by measuring a $^{13}CO_2$ line at 2209.77 cm^{-1} with the CRDS and using the same line fitting method as for the radiocarbon spectra. The concentration of i = C14 or i =

CO_2 is calculated from the absorption line area using equation: $C_i = (A_i k_b T)/(S_{oi} p)$, where A_i is the absorption line area, k_b is the Boltzmann constant, T is the sample temperature, S_{oi} is the absorption line strength and p is the sample pressure. The $^{14}C/^{12}C$ concentration was calculated as C_{C14}/C_{CO2} ratio.

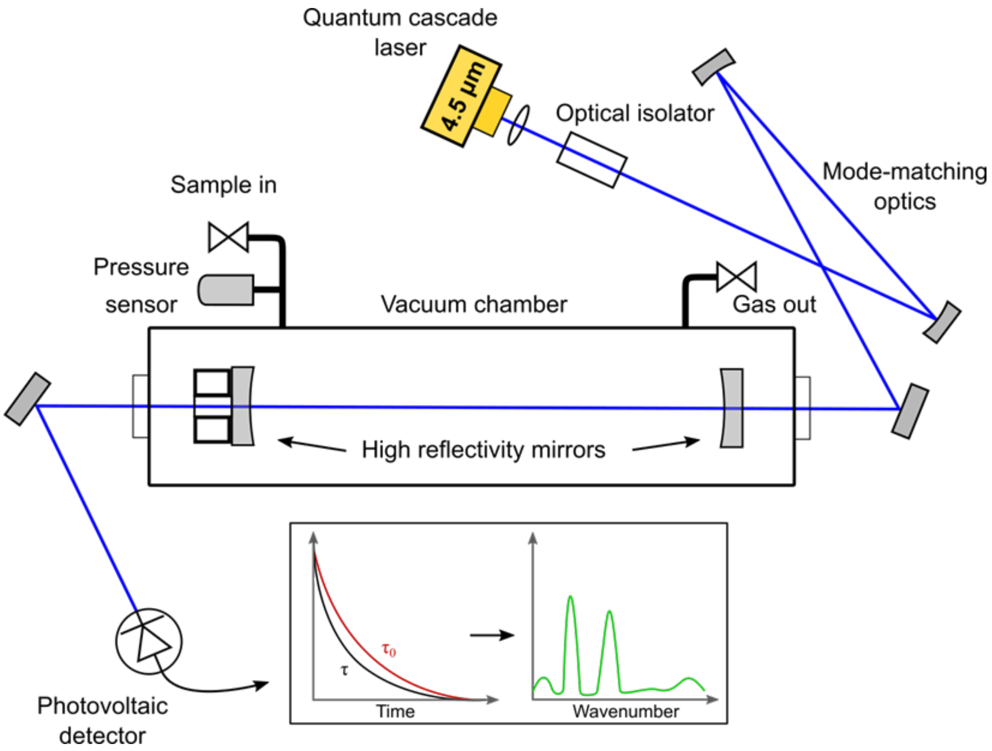


Figure 11. Schematic of the CRDS arrangement used for ^{14}C outgassing measurements.

The CRDS measurement requires concentrating the CO_2 to enable detection of low ^{14}C concentrations at good accuracy. Therefore, an on-line sample processing unit was built for the CO_2 purification and used together with the CRDS. The sample processing unit is shown in Figure 12, and detailed information of the sample processing unit is given in Ref [5].

The sample processing unit takes in samples in gas phase. A diaphragm pump is used to flow the air through the sample processing unit. The gas flows through a particle filter to a catalyser, which converts methane and other hydrocarbons to CO_2. The conversion occurs on palladium catalyst which is kept at 500 °C temperature. The preparation of catalyst is presented in more detail in Ref [8]. Conversion of hydrocarbons to CO_2 allows detecting ^{14}C also originally present in other molecular species than CO_2 (such as methane). The catalyser can also be bypassed to get the ^{14}C content only in CO_2. After the catalyser, a Vaisala GMP343 carbon dioxide sensor is used together with a pressure sensor to detect the CO_2 content in the sample air. A mass flow controller adjusts the flow speed, and solenoid valves guide the sample flow to one of two identical CO_2 traps. The two traps are used sequentially so, that when one trap is releasing trapped CO_2, the sample air is flown through the other trap that collects new CO_2 sample. The traps are made of aluminium blocks made into form of heat sinks. The trapping material, Lewatit VP OC 1065 ion-exchange resin from Lanxess, is positioned inside a drill hole made into the blocks. The resin adsorbs CO_2 selectively from air at room temperature. The CO_2 is released to the CRDS cell from the resin by heating the trap over 50 °C temperature. The heating is achieved with resistive heaters. After the CO_2 release, the trap is cooled back to room temperature with fans. The trapping time depends on the CO_2 concentration of the sample air, but typically 30 minutes was the minimum time to gather enough CO_2 for the CRDS measurement.

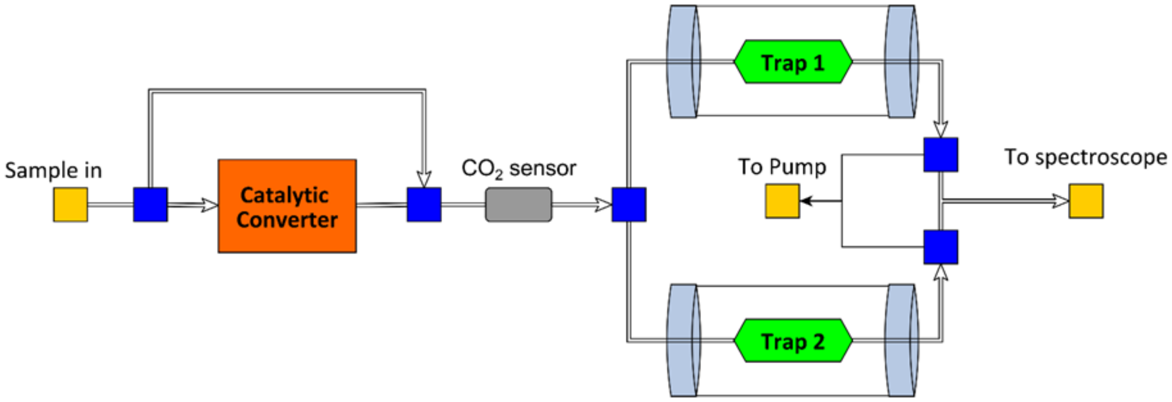


Figure 12. Sample processing unit.

2.3.1 Comparison between CRDS and LSC of graphite measurements at VTT

The same graphite samples were analysed with both CRDS and LSC. For CRDS, the measurements on the graphite pieces were started with total combustion of a sample, which was possible by heating the sample in a catalytic pyrolyser up to 800 °C. In the pyrolizer (from Raddec International) the graphite samples are converted into carbon dioxide to enable measurement by CRDS. The produced carbon dioxide was flown through and trapped with the sample processing unit and released to the CRDS for ^{14}C detection, as shown in the schematics in Figure 13. The pyrolyser has two sample zones in serries followed by an oxidising catalyser. The catalyser contains 0.5 % platina-alumina pelletised catalyst, which is heated to 800 °C. The graphite samples were loaded on silica-glass boats and positioned in the sample zone 1, which is the first sample zone after the air inlet to a silica-glass tube enclosing the sample zones and the catalyser. In the measurements, sample zone temperatures of 20 – 800 °C were used. A synthetic air cylinder was connected to the pyrolyser air inlet to feed in CO_2-free air. After first graphite combustion tests, a suitable synthetic air mass flow of 0.40 l/min at the sample processing unit mass flow controlled was adjusted for the experiments. The first part of the heating program, from room temperature to 500 °C in 35 minutes, resulted to only small amount of CO_2 output from the sample. The CO_2 captured by the sample processing unit, and released after the trapping to the CRDS cavity, was insufficient to make a ^{14}C detection with CRDS. The second stage of the pyrolyser program: the heating from 500 °C to 800 °C in 35 minutes, resulted in clearly higher CO_2 output and allowed detection of ^{14}C with good accuracy. A graph showing the sample zone temperature and the CO_2 output as function of time is shown in Figure 14. Heating the graphite gradually results in exponentially growing CO_2 output, which reaches its maximum above 750 °C sample temperature. It is, however, possible that the maximum output occurs already at lower temperature, but because of the delay from the gas reaching the CO_2 sensor the CO_2 value is lagging behind. In the combustion measurement shown in Figure 14, the CO_2 reaches almost 20000 ppm. The maximum CO_2 output depended on the amount of graphite sample used in the combustion. From three graphite samples labelled: #1, #4 and #5, two or three samples of each were weighted, combusted, and measured with CRDS. The results are presented in Figure 15.

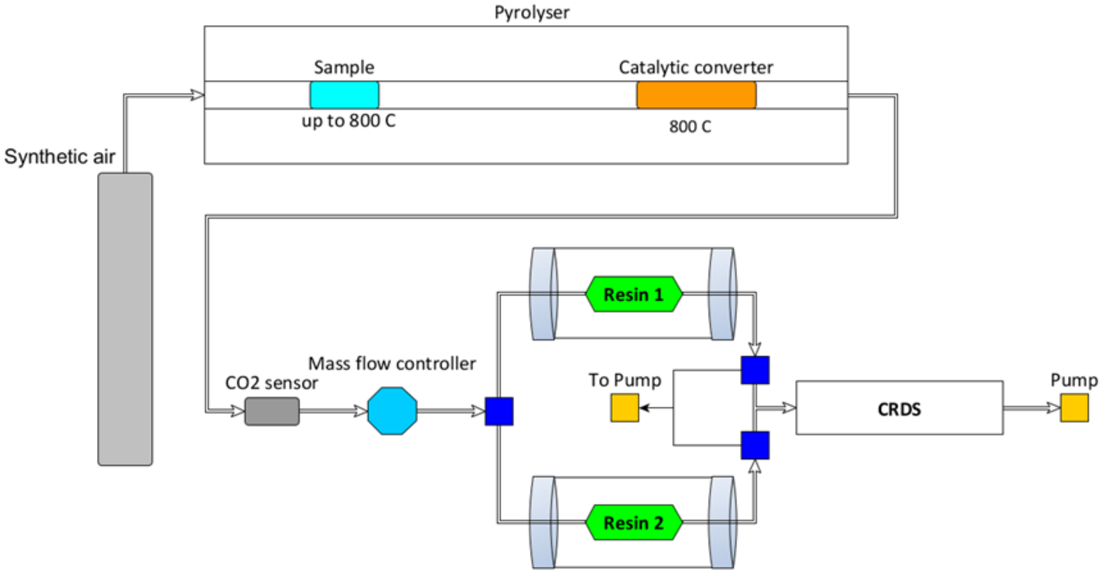


Figure 13. Schematics of pyrolyser experiments. The air flow through the system was controller with a regulator and a needle valve at the synthetic air cylinder outlet and the mass flow controller in the sample processing unit. The catalytic converter of the sample processing unit was bypassed to reduce flow resistance in the system.

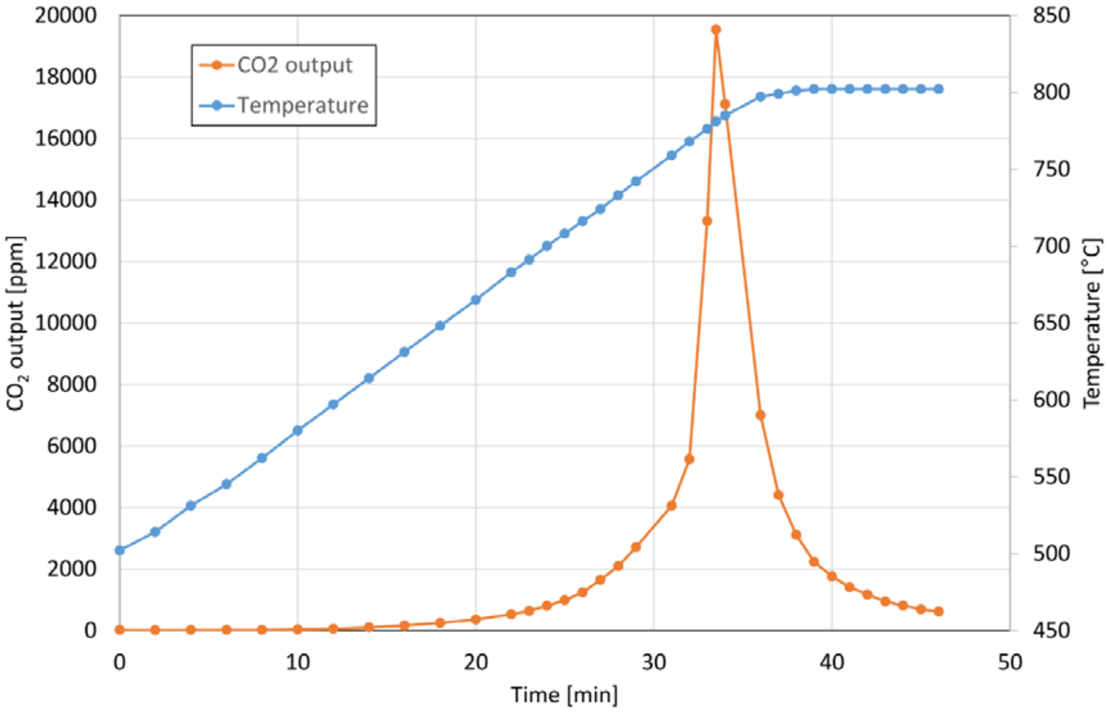


Figure 14. CO_2 output and sample temperature relation. Constant temperature gradient results in exponential CO_2 output above 700 °C, which ends quickly, when most of the sample is combusted.

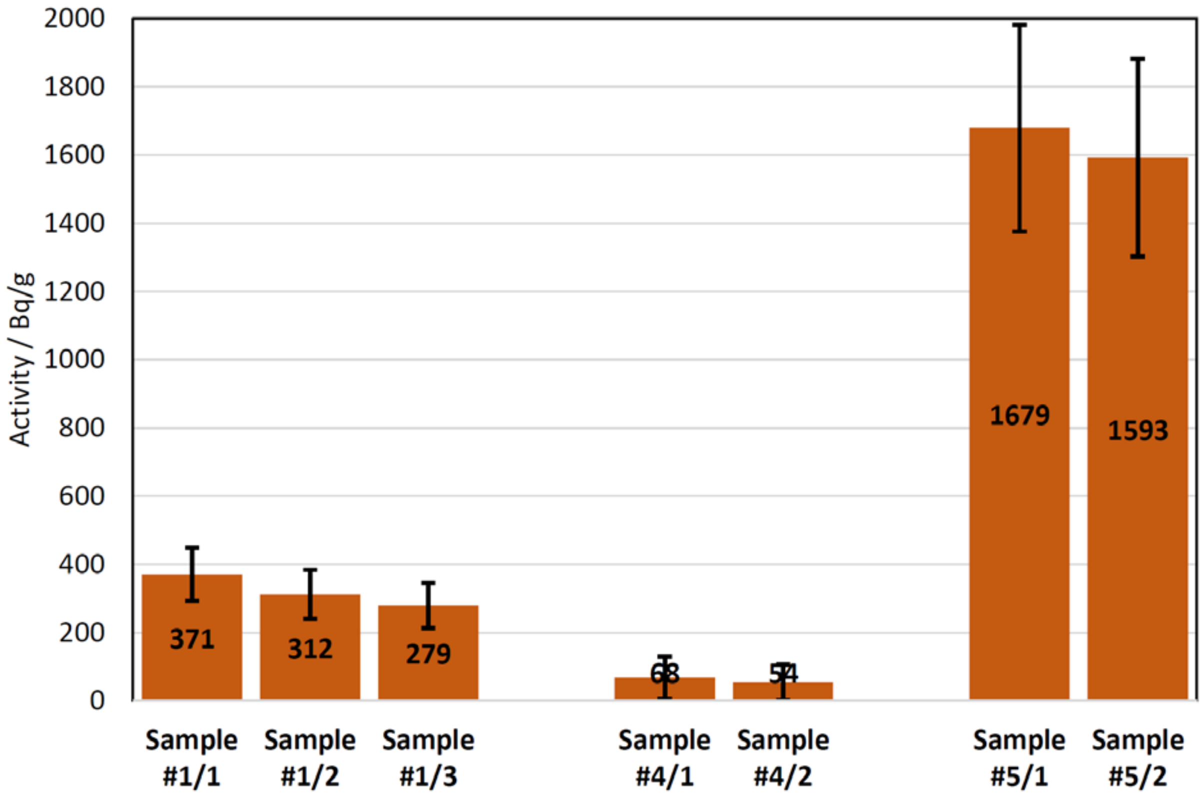


Figure 15. Activities in the irradiated graphite samples. Three measurements were done from sample #1 and two measurements were done from each of the samples #4 and #5. The measured ^{14}C activities in Bq/g are shown on the columns and the error bars are shown on the top of the columns.

There is little variation between the measured ^{14}C activity concentration within single samples. The variation is mostly due to variation of the actual activity within the graphite, which depends on the location on the graphite block. In addition, the distance from the graphite block surface affects the activity, as the radiation is strongest at the surface.

The same samples have been characterised by LSC 15 months earlier. The amount of C14 was determined by a procedure combining radiochemistry and LSC. First a complete destruction of the solid matrix was done followed by radiochemical separations of the analytes and purifications from interfering radionuclides. The overall procedure[6] comprised of an oxidative acid digestion (HNO3:H2SO4:HClO4) in which carbon was oxidised to CO_2, which was then absorbed into a NaOH solution. The measurement of C-14 was carried out using Wallac 1415 Liquid Scintillation counter. Samples were mixed into HiSafe 3 scintillation cocktail. The yields of 14C analysis were experimentally estimated using 14C spiked graphite samples. More details for this analysis are presented in Ref [7].

The measured activity by LSC of sample #1 was 196 Bq/g, of sample #4 19.9 Bq/g and of sample #5 1571 Bq/g while the average value of the CRDS measurements was 321 Bq/g, 61 Bq/g and 1636 Bq/g, respectively. The C-14 activities measured with CRDS were higher than what was measured with liquid scintillation counting (LSC), especially for lower activity concentrations. However, the method use for the LSC analysis was based on wet oxidation and is known to not provide 100% efficiency. Further investigations are therefore needed to validate the LSC measurements, for instance by using a more efficient method where the oxidation is carried out in a pyrolizer. Nevertheless, this comparison shows that CRDS is able to give results that are similar to the LSC measurements and that the method can be a valid alternative to currently used techniques.

3. Comparison between LSC and CRDS

Worldwide there are over one hundred traditional radiocarbon laboratories that mainly use LSC, Liquid Scintillation Counting, for many analytical purposes, a few dozen using AMS Accelerator Mass Spectrometry and very few laboratories that use, in the field of nuclear research, CRDS, cavity ring down spectroscopy. VTT has developed the method especially for applications related to monitoring in nuclear facilities[5], [9], [10]. A few other groups worldwide have developped the CRDS method for C14 detection[11]–[14], with extremetely high sensitivity down to a few ppq achieved in the laboratory[15].

Considering the parameter needed by the LSC and CRDS techniques and their relative performance it is possible to compare them as shown in table 1.

Table 1 – Comparison between LSC and CRDS techniques.

Characteristic of the technique	**LSC**	**CRDS**
Physical properties used for C-14	β-decay counting	Photon absorption
Material into which a sample is to be transformed for analysis	CO_2 – C_6H_6	CO_2
Sensitivity	Very high (down to ptt, parts per trillion)	High (down to ppb parts per billion)
Possible interferences	Cosmic Ray	$^{13}C^{16}O_2$, N_2O, O_3
Precision	High	high
Analysis cost	High (600 € C_6H_6)	Low (almost zero)
Labour cost	High (manual work needed)	Low (can be automated)
Instrument cost	High (300 KEuro) including the benzene synthesis pipeline	~100 k€ (including sampling)
Technique footprint	50 m^2	1-2 m^2 (including sampling)
Analysis duration	15 – 20 hours	5 min
Sample preparation time	1 – 3 days	30 min

4. Conclusions

The CRDS and the LSC measurements have both their benefits in radiocarbon measurements, but also limitations. To reach the best measurement performance, the technique should be selected between the two methods depending on measurement circumstances and requirements.

The LSC gives reliable and high accuracy results down to parts per trillion $^{14}C/^{12}C$ concentrations, when long detection time can be used. The sample needs to be dissolved to LSC media to enable the measurement. The technique thus requires taking the sample to laboratory for proper sample preparation for the measurement. The benefit of the LSC is that with a single device, many different radioactive species can be detected, not only radiocarbon. Downside is that sometimes a signal of different radioactive species can overlap with the radiocarbon signal, and thus increase the uncertainty of the measurement.

The CRDS method can currently reach 0.2 part per billion $^{14}C/^{12}C$ concentration detection limit in field measurement. Unlike LSC, the CRDS measurement can be done automatically in field conditions. The CRDS measurement is done with sample in gas phase, which enables using automated sample processing unit. The sample processing unit can take gaseous sample directly from air, and currently the sample rate is one sample every 45 minutes. Also, liquid, and solid samples can be measured by connecting the CRDS measurement with an oven or pyrolizer to combust the samples into gas phase. The CRDS measurement can differentiate between radiocarbon in different molecular species, such as carbon dioxide and hydrocarbons. The CRDS technique made for radiocarbon measures only radiocarbon and no other radioactive species, which prevents other species disturbing the measurement. Only limiting factor is high concentrations of N_2O, which needs to be removed from the sample gas.

The LSC works the best, when low detection limit is required, and sample can be prepared properly for the measurement. The CRDS performs better in field measurements, in continuous monitoring, and where flexibility of the measurement is important, or information of the radiocarbon speciation in different carbon species is required.

5. References

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