CArbon-14 Source Term
CAST

Definition of the analytical strategy for 14C measurements (D3.7)

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CAST – Project Overview

The CAST project (CArbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), irradiated graphite and from ion-exchange materials.

The CAST consortium brings together 33 partners with a range of skills and competencies in the management of radioactive wastes containing carbon-14, geological disposal research, safety case development and experimental work on gas generation. The consortium consists of national waste management organisations, research institutes, universities and commercial organisations.

The objectives of the CAST project are to gain new scientific understanding of the rate of release of carbon-14 from the corrosion of irradiated steels and Zircaloys and from the leaching of ion-exchange resins and irradiated graphites under geological disposal conditions, its speciation and how these relate to carbon-14 inventory and aqueous conditions. These results will be evaluated in the context of national safety assessments and disseminated to interested stakeholders. The new understanding should be of relevance to national safety assessment stakeholders and will also provide an opportunity for training for early career researchers.

For more information, please visit the CAST website at:
http://www.projectcast.eu

CAST		
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Document title
Definition of the analytical strategy for ^{14}C measurements

Executive Summary

The objective of Task 3.2 is to determine the forms of 14C (organic/inorganic, partition in solution) leached into solution from Zircaloy fuel cladding hulls recovered after the industrial treatment process to dissolve the spent fuel. To achieve this goal, analytical methods must be developed in order to answer to different objectives:

- Determine carbon mass balance;
- Have information on the molecular weight of molecules present in samples;
- Have a semi-quantitative distribution of the different chemical families (alcohols, ketones, carboxylic acids, etc…).

Experiments will be conducted on several types of hulls: Zircaloy or M5 cladding.

The analytical protocol will be realised as follows:

1- Development of method for quantification of total organic carbon with the aim to determine the carbon mass balance for each leachate solution.
2- Development of spectroscopic methods such as infrared-red analysis to identify the main families of chemical functions (carboxylic acids, aromatic compounds, ketones, alcohols, etc…).

3- Development of analytical methods based on chromatographic techniques. The aim is the detection and quantification or semi-quantification of targeted families of molecules. For example, ion chromatography will be used for the detection of small carboxylic acids and a coupling between gas chromatography and mass spectrometry will be used for detection of small organic compounds with high polarity.
4- Development of analytical methods based on mass spectrometry (electrospray-mass spectrometry technique) with the aim to detect and identify molecules with high molecular weight.

This deliverable presents the analytical strategy and the procedures associated with the analytical techniques.

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1 Analytical strategy

The goal is to determine the source term of ^{14}C and its speciation as released from Zr wastes. Leachates simulating a cementitious environment (NaOH solution, pH 12) from irradiated Zr fuel claddings will be analyzed to allow detection and quantification of organic compounds in solution. No study will be carried out on gas.

The aims of this analytical strategy are to answer to different objectives:

- Have information on the molecular weight of molecules present in samples
- Have information on chemical structure (or chemical family) of molecules
- Have a semi-quantitative distribution of the different chemical families (alcohols, ketones, carboxylic acids, etc…)

The experimental protocol will be realized as follows:

1- Development of method for quantification of total organic carbon with the aim to determine the carbon mass balance for each leachate solution.
2- Development of spectroscopic methods such as infrared-red analysis to identify the main families of chemical functions (carboxylic acids, aromatic compounds, ketones, alcohols, etc…).
3- Development of analytical methods based on chromatographic techniques. The aim is the detection and quantification or semi-quantification of targeted families of molecules. For example, ion chromatography will be used for the detection of small carboxylic acids and coupled gas chromatography / mass spectrometry (GC/MS) will be used for detection of small organic compounds with high polarity.
4- Development of analytical methods based on mass spectrometry (electrospray-mass spectrometry technique) with the aim to detect and identify molecules with high molecular weight.

This analytical strategy has been already demonstrated for the study of the uranium carbide dissolution [LEGAND ET AL., 2014].

2 Analytical methods

The sample delivery in the analytical laboratory is dependent on the activity. A first dilution of samples could be necessary to respect the acceptance in alpha and gamma activities and handling in the laboratory (at the risk to be below detection limits of 14-carbon species).
In a second step, research and analysis of organic targeted molecules will be developed. In this aim, a convenient analytical approach for sample analysis in highly concentrated media such as water cement solution has to be developed as presented in Figure 1.

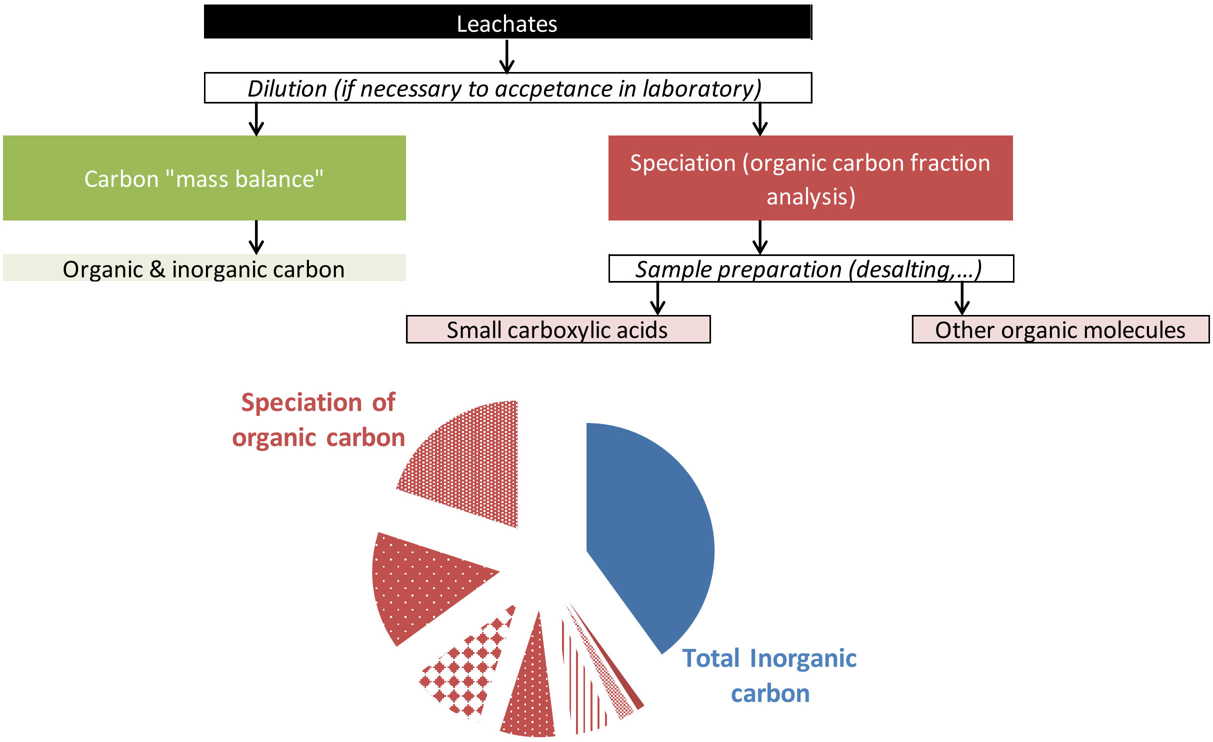


Figure 1: Analytical strategy (green colour represents total carbon, red represents the organic carbon and blue the inorganic carbon).

2.1 Carbon mass balance

2.1.1 Total, organic and inorganic carbon

The quantification of total organic carbon is realized to know the quantity of organic matter which was leached in solution. This quantification will also help at the end of the development of the analytical protocol to control the mass balance of each sample (Figure 2).

The used TOC analyzer is a Bioritech 1010. The measurement is realized by a chemical oxidation. The sample is injected into a chamber with phosphoric acid (acid attack gives total inorganic carbon (TIC)) followed by sodium persulfate producing an oxydation reaction given total organic carbon (TOC). The organic matter is oxidized in CO_2, which is quantified by in-frared technique. Thus, a differentiation between organic and inorganic carbon will be realized.

Figure 2: TOC analyser in a glove box.

2.1.2 Total ^{14}C determination

Pyrolysis will be used to extract ^{14}C, using a tri-tube pyrolysis furnace (Figure 3) manufactured by ERALY et associés (Noisy le Roi, France).

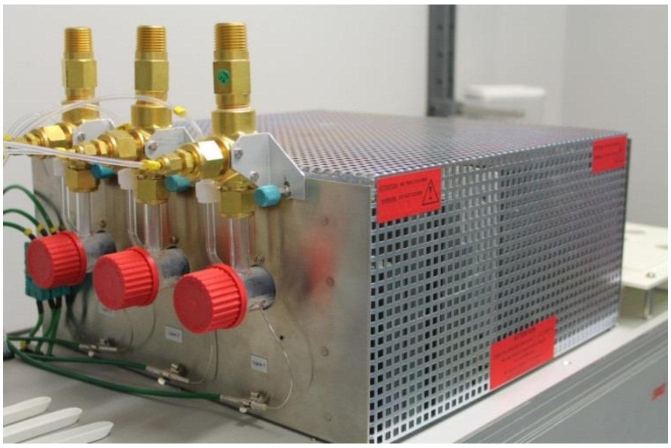


Figure 3: Tri-tube pyrolysis furnace.

The furnace has two independent heating zones. The first one, where the sample is placed, is programmable (temperature gradient) whereas the second heating zone remains at 950°C. The sample in the first zone is swept by a nitrogen stream during the heat-up, while the second zone is swept by a stream of N_2 plus O_2, in order to guarantee the complete combustion of the gases released during the pyrolysis taking place in the first zone. The gas flow rate is 150 mL/min in both zones. The leachate sample (between 0.1 and 0.5 ml) will be placed into the cold furnace in ceramic boats (Figure 4).

Figure 4: Porcelain boat.

As the temperature rises, the given off gases are trapped first with ^{3}H extracted in a bubbler (HCl 0.1M), followed by ^{14}C trapping in bubblers 2 and 3 (NaOH 0.2M) (Figure 5).

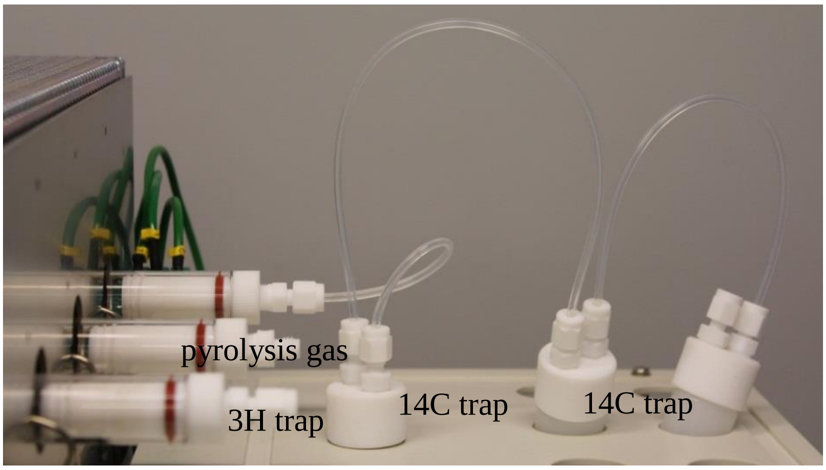


Figure 5: System to trap the pyrolysis gases.

The applied temperature gradient is shown in Figure 6. The temperature program had been optimized to ensure a recovery of both 3H and 14C above 90% for liquids samples.

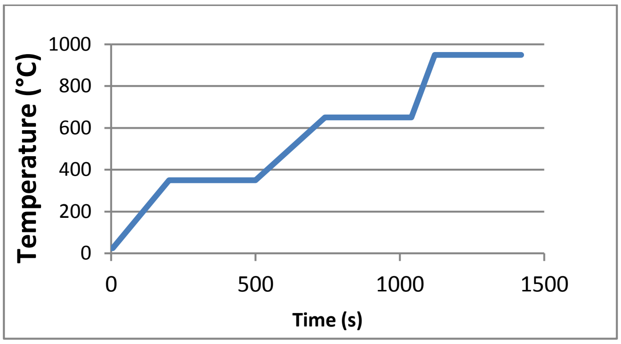


Figure 6: Temperature program used for leachate solution pyrolysis.

^{14}C trapped in the NaOH solution can be measured by liquid scintillation counting on a Tricarb 2910TR apparatus calibrated by the establishment of a quenching curve. In our conditions, at the limit of detection (around 0.3-0.5 Bq/ml of sample in the ceramic boat), we can also prepare from the trapped solution an appropriate precipitate ($CaCO_3$ for example) that can then be sent to the CEA/LMC14 in the Saclay center to measure ^{14}C by AMS (Accelerator Mass Spectrometry).

2.1.3 Organic and inorganic ^{14}C partition

Such a partition has never been done in our laboratory. Based on the reaction used to make organic/inorganic partition in commercial apparatus, we propose to treat a small volume of the leachate solution (1 ml for example) with a solution of H_3PO_4 25 % under N_2 bubbling to lead the CO_2 produced (inorganic C) in a trap solution (NaOH). Organic carbon will be retained in the reaction vessel.

Then, we can take an aliquot of the trap solution and measure it by LSC (Liquid Scintillation Counting) to determine the inorganic ^{14}C. We can then pyrolyse the solution remaining in the reaction vessel to measure the organic ^{14}C as previously described.

This procedure will be tested on a mix of two labelled molecules (one organic, for example glucose and one inorganic molecule carbonate for example). If this procedure does not prove successful we will be only able to give the total ^{14}C content in the leachate solution. If the result from LSC is below the limit of detection, AMS measurement will be planned.

2.2 Organic carbon speciation

2.2.1 Sample preparation

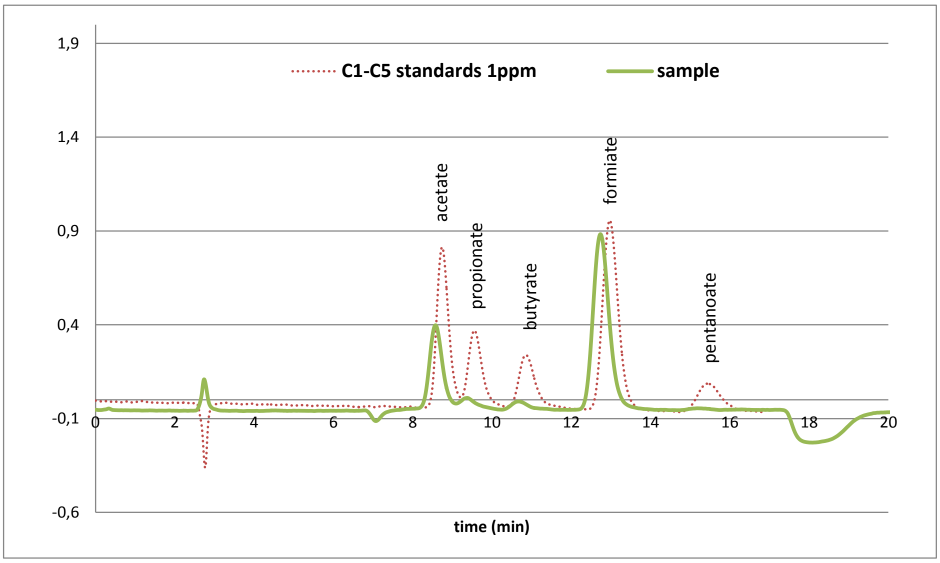
After determination of the amount of organic carbon, further analytical techniques will be applied. However, the leachates simulate a cementitous environment (NaOH solution). A desalting and pre-concentration step is therefore necessary before analysis. For this, ion exchange resin will be used (PS/DVB anion exchanger in H^+-form, Macherey-Nagel). The aim is to exchange Na^+ ions with H^+ from the resin. After washing of the resin, samples are loaded onto the column and then eluted in water. Samples can then be evaporated under nitrogen atmosphere, allowing the evaporation of water. At the end of this treatment, the sample is available to be dissolved in different solvents according to the different analytical techniques requirements.

2.2.2 Fourier transform infrared

FTIR spectroscope (Vector22, Bruker) will be used to identify functional groups of organic compounds present in solution (carboxylic acids, aromatic compounds, ketones, etc…) and then to guide the choice of analytical methods to implement thereafter. A development of the technical method has to be done. Calcium fluoride (CaF_2) plate will be used. CaF_2 is an IR-windows material insoluble in water. It is compatible with most acids and bases and presents a good transmission between 900–4,000 cm^{-1} in our configuration. The limit of detection and solution volumes will depend on samples matrix (NaOH solution, organic solvents, etc…).

2.2.3 Ion chromatography

Ion chromatography can quantify small carboxylic acid. A protocol has already been developed in the laboratory for the detection of carboxylic acids from C_1 to C_5 in high NaOH concentrations. An example of a real sample chromatogram in NaOH solution and the ion chromatography in glove box are presented in Figure 7.



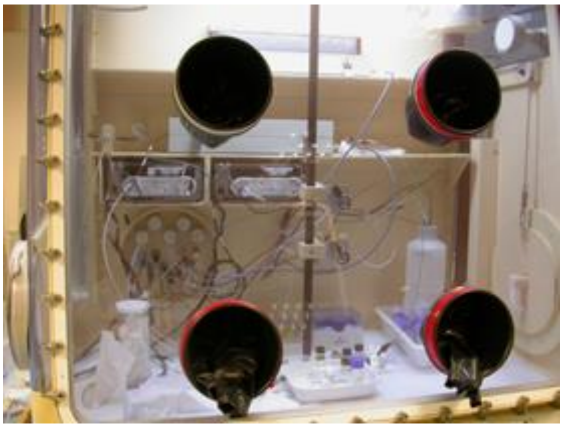


Figure 7: Example of chromatogram and ion chromatography in glove box.

Our ion chromatography is equipped with a conductometric detector (ICS 3000 High Performance Ion Chromatography System, Thermo Scientic equipped with an ICS-3000 DP Dual Pump module, an ICS-3000 EG Eluent Generator, an ICS-3000 AS Autosampler, an ICS-3000 DC Detector/Chromatography module and an ASRS 4 mm suppressor controlled by the Chromeleon software). However this detector does not detect whether carboxylic acids are marked with ^{14}C or not. To overcome this issue, it is planned to add a scintillator counter as a new detector on the ion chromatography.

2.2.4 Gas chromatography coupled with mass spectrometry

Identification of low mass volatile molecules is done by gas-chromatography coupled with mass spectrometry (Figure 8). Different capillary columns with different polarity can be used to increase the number of identified molecules.

The ion source used here for mass spectrometry detector is electron impact (Trace GC coupled with Trace DSQ mass spectrometer, Thermo Scientific). The analytical conditions are standard in order to be able to use mass spectra library to help for identification of molecules.

Figure 8: Gas chromatography-coupled with mass spectrometry.

To increase the number of identified molecules, selective extraction of molecules families can be realized before GC/MS analysis. For this, after the evaporation process, the sample can be dissolved in different solvents, *e.g.* a polar solvent for the extraction of more polar molecules or hexane for extraction of non-polar molecules.

When molecules of interest or family of molecules of interest are detected, a semi-quantification can be realized in the same analytical conditions using gas chromatography coupled with flame ionization detector (FID) (Trace GC, Thermo Scientific). The semi-quantification can be realized with internal or external standards if chromatograms are too complicated.

Thus, gas chromatography analysis will help for molecule identification after coupling with mass spectrometry and for quantification after coupling with FID. The limit of detection of our GC/FID is usually of 1 ppm in case of complex mixtures but can also depend of the sample complexity (mixture of organic molecules in NaOH solution).

2.2.5 Electrospray-mass spectrometry analysis

For the detection of molecules with molecular weight higher than one hundred g/mol, electrospray-mass spectrometry (ESI-MS) technique can be used (Figure 9) (Nano-ESI mass spectrometer equipped with a quadrupole mass analyzer, Micromass). The sample is introduced into a nano-capillary. By application of a high voltage on this capillary, analytes are transferred as ions in an aerosol. After desolvatation (i.e. solvent evaporation) a stream of charged ions are produced. They are afterwards transferred in the mass analyser, a quadrupole. This ambient pressure soft ionization technique allows the detection of intact polar molecules with higher molecular weight than GC/MS technique in complex mixture [PLANCQUE ET AL., 2001]. ESI is also widely applied in studies of non-volatile organic compounds, thermally labile inorganic compounds and biomolecules, which are difficult to analyse using EI source.

In a similar manner with preparation for gas chromatography, different solvents can be used for selective extraction of molecules. ES-MS can then be used for the identification of molecules present in solution.

For molecules with molecular weight lower than 1000 g/mol, the resolution on the mass spectrum can be sufficient and help for determination of the $^{12}C/^{14}C$ ratio. The detection of molecules marked with ^{14}C can also be realized. However the concentration of ^{14}C has to be quite high with this analytical technique and different tests for detection limit purposes on standard molecules have to be realized before.

Figure 7: Electrospray-Mass spectrometry.

3 Conclusions

The different objectives of this study and the analytical techniques are summarized in Table 1.

Aim	**Analytical techniques**
Mass balance ^{13}C and ^{14}C	COT
Qualitative analysis for determination of chemical families	IRTF-spectroscopy
Quantification of carboxylic acids	Ion chromatography Gas chromatography-mass spectrometry
Detection of low mass molecule	Gas chromatography-mass spectrometry
Detection of molecules with higher molecular weight	ESI-MS

Table 1: Analytical techniques and associated goals.

If main of the analytical equipment are in gloveboxes (IC, ESI-MS, COT Analyzer), IRTF-spectroscopy, GC/MS and GC/FID are in chemical hood. The ability to handle active samples in gloveboxes or in chemical hood depends on general rules of CEA, according to each radio-nuclides present in the sample and their activity.

References

LEGAND, S., BOUYER, C., CASANOVA, F., LEBEAU, D., AND LAMOUROUX, C. 2014. Uranium carbide dissolution in nitric acid: speciation of organic compounds. *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 302, 27-39.

PLANCQUE, G., AMEKRAZ, B., MOULIN, V., TOULHOAT, P., AND MOULIN, C. 2001. Molecular structure of fulvic acids by electrospray with quadrupole time-of-flight mass spectrometry. *Rapid Communications in Mass Spectrometry*, Vol. 15, 827-835.