

Carbon-14 Source Term

CAST



REPORT ON ^{14}C DISTRIBUTION IN IRRADIATED GRAPHITE FROM THE RESEARCH REACTOR VVR-S USING ACCELERATOR MASS SPECTROMETRY AND BETA IMAGING (D5.7)

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CAST – Project Overview

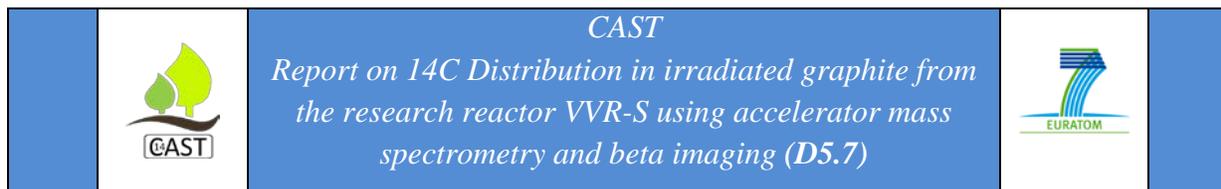
The CAST project (Carbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14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



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REPORT ON 14C DISTRIBUTION IN IRRADIATED GRAPHITE FROM THE RESEARCH REACTOR VVR-S USING ACCELERATOR MASS SPECTROMETRY AND BETA IMAGING (D5.7)

Executive Summary

The main objective of the IFIN-HH in the second year of its input to Work Package 5 was to update the inventory of 14C in the irradiated graphite arising from thermal column of VVR-S Reactor and radioactive wastes containing organic and inorganic 14C compounds. IFIN-HH has characterized the 14C inventory of irradiated graphite from thermal column of VVR-S Reactor, and has started to develop a method, based on the use Accelerator Mass Spectrometry (AMS) which will be suitable to characterize the distributions of 14C inventory in irradiated graphite. Finally, in order to measure the total release of 14C (and 3H) to solution and gas from crushed and intact i-graphite from the VVR-S Reactor, the experimental apparatus has been designed and manufactured.

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1 Introduction

Irradiated graphite at IFIN-HH

Generally, ^{14}C is produced in all types of reactors, mainly through neutron-induced reactions with isotopes of carbon, nitrogen and oxygen. The precursor nuclides of most significance to the production of ^{14}C are ^{13}C , ^{14}N and ^{17}O . They are present in the fuel, fuel cladding, coolant, moderator and structural materials of the reactor. The mechanisms and cross sections for the reactions of interest are listed for different neutron energy regimes in Table 1.

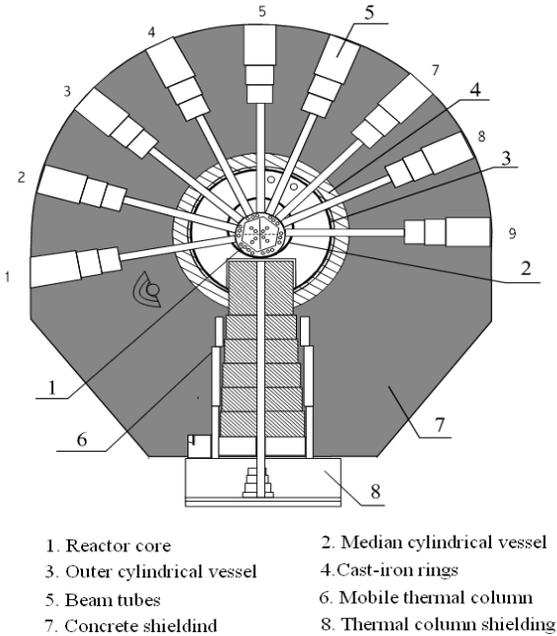
Table 1 Neutron activation reactions and cross sections for the production of ^{14}C for different neutron energy regimes.

Neutron induced reactions	Natural isotope abundance of target element	Cross section (barn)		
		Thermal	Resonance integral	Fission
$^{17}\text{O} (n, \alpha) ^{14}\text{C}$	0.038%	0.235	0.106	0.095
$^{14}\text{N} (n, p) ^{14}\text{C}$	99.6%	1.83 ± 0.07	0.818	0.0355
$^{13}\text{C} (n, \gamma) ^{14}\text{C}$	1.1%	$1.37\text{E-}03$	$5.93\text{E-}04$	$5.16\text{E-}05$

The inventory of i-graphite at IFIN-HH is going to be actualized and it stems from the thermal column of the VVR-S Reactor. The overwhelming amount of ^{14}C is located in the thermal column of the VVR-S Reactor. The mass of i-graphite of the thermal column is estimated to be 5.3 metric tonnes. In addition there is more than $6\text{E}10$ Bq of ^{14}C contained in organic and inorganic compounds as radioactive wastes stored at the Radioisotopes Production Centre from IFIN-HH.

The VVR-S nuclear reactor from IFIN-HH is a research reactor with a maximum thermal power of 2 MW moderately cooled and reflected with distilled water, and fueled with enriched uranium (10% in the beginning and 36% subsequently). It was commissioned in 1957 and dedicated to nuclear physics research and radioisotopes production. Until 1984 the reactor was operated with nuclear fuel type EK-10 (10% enrichment) and from 1984, this fuel was replaced by S-36 (36% enrichment). The reactor was operational until 1997 when the reactor was definitively shut-down. On average, the reactor was operated 5 days per week at full or variable power levels. During 40 years of operation, the VVR-S reactor produced 9.59 GWd. The maximum flow of the thermal neutrons was $2\text{E}13$ n/cm²s.

A horizontal and vertical cross section of the reactor core is presented in Figures 1 and 2.



VVR-S REACTOR HORIZONTAL CROSS-SECTION

Figure 1: Horizontal cut-view through the VVR-S reactor

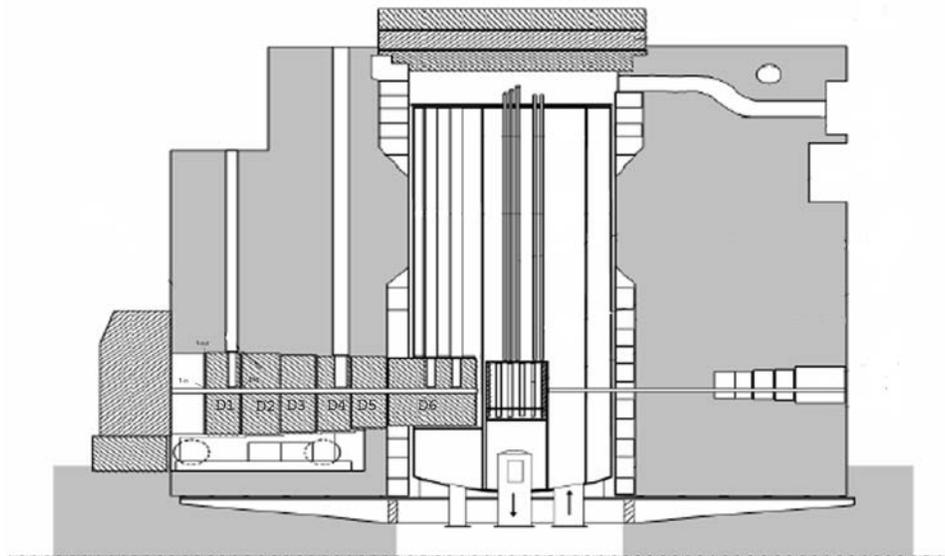


Figure 2: Vertical cut-view through the VVR-S reactor and the movable thermal column with its 6 discs

The irradiated graphite grades, which are investigated in IFIN-HH, have been taken from thermal column of the VVR-S Research Reactor. The mobile thermal column (Figure 3) is made of 6 graphite discs placed on a mobile truck. Graphite discs are installed into a 20 mm wall thickness aluminium cylinder. Initially, the thermal column was provided with a cooling system that axially penetrated the graphite plate connected to the water-cooling system. On the basis of subsequent operational experience, it was concluded that this system is not necessary; it was not used any further. Therefore, the horizontal tubes of the cooling system were filled with nuclear grade graphite rods of the same type as the discs of the thermal column. Samples have been collected from these graphite rods and the surrounding graphite sleeve of the central graphite rod (Figure 4).



Figure 3: Thermal column



Figure 4: Thermal column disc 6

The goal of these experiments was to determine the ^{14}C accumulation during the operational time of about 50 years in the thermal column of VVR-S Reactor in IFIN-HH-Bucharest and, also, ^{14}C surface activity. Samples for these determinations were collected after the final shut down and fuel removal of the reactor core.

2 Materials and Methods

2.1 VVR-S reactor thermal column

Each graphite disc is enclosed in thick (3mm) aluminium cover. The dimensions are: Disc diameter: 1000-1150 mm, central inner opening 100 mm diameter and height 400 mm. The entire active thermal column is about 3m long. Table 2 records mass and dimension data for the 6 graphite discs.

Table 2: Graphite discs masses and dimensions

Disc	Diameter (cm)	Length (cm)	Graphite mass(kg)
1	115	40	715
2	110	40	660
3	110	40	670
4	105	40	595
5	105	40	610
6	100	100	1360

The nearest disc to the reactor core is number 6 (see Figure 4). During reactor operation the central tube of the cooling system was filled with a graphite rod (8 cm diameter) covered by a 1 cm thick cylindrical graphite sleeve for column discs 1-4 and a graphite rod (diameter 10 cm) for column discs 5 and 6, which sealed the entire central opening. The other horizontal tubes of

the cooling system have been filled (only for discs 5 and 6) with graphite rods of 4.4 cm diameter.

Sampling was performed from several positions inside and outside the graphite sleeve of the central rod for discs 1-4 and from small graphite rods located around the central graphite rod for discs 5 and 6. For the discs 5 and 6, two pieces of i-graphite have been cut from the graphite rods, to facilitate easier handling in the radiochemical laboratory. One piece was cut from rod's edge nearer the reactor vessel (**Sample 6.1, Sample 5.1**) and the other piece from the opposite part of the rod (**Sample 6.2, Sample 5.2**). From each piece collected from graphite rod located inside the disc 6, two separate samples have been taken (Sample 6.1-1, Sample 6.1-2, Sample 6.2-1 and Sample 6.2-2) (Figure 5).

Figure 6 provides further information on the thermal column itself, including the position of disc number 6.

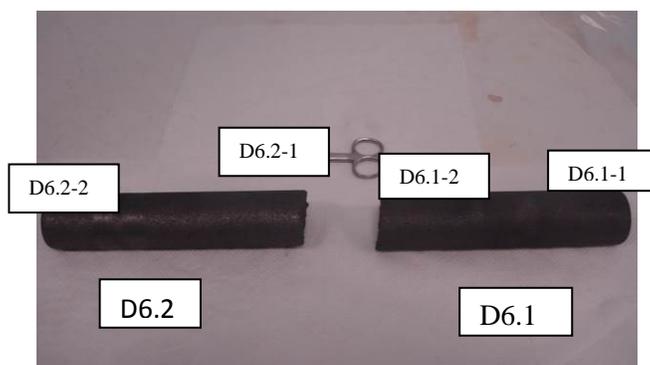


Figure 5: Irradiated graphite samples collected from small rod in disc 6

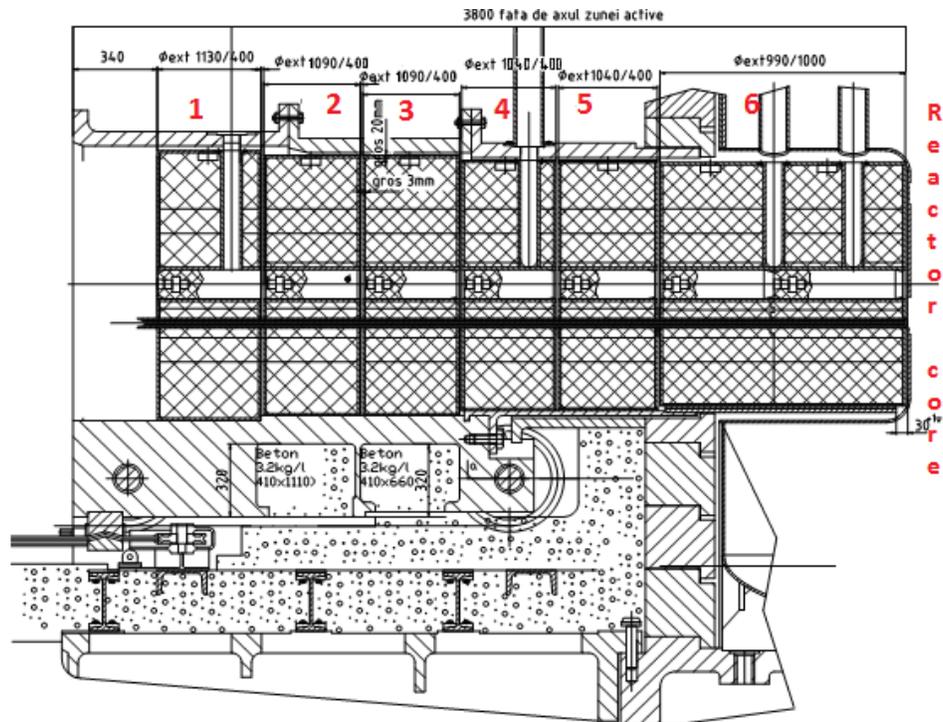


Figure 6: VVR-S thermal column cross section

2.2 Irradiated graphite samples preliminary characterisation

The estimation of the radionuclide inventory of the i-graphite has been determined by gamma spectrometry using an Ortec Gamma HPGe detector type GMX. For radionuclides that are problematic to detect, the specific and the total activity of ^3H and ^{14}C in the i-graphite of thermal column components have been calculated by means of the scaling factors method using ^{60}Co as the reference radionuclide and the thermal neutron flux distribution in space, according to the data from the literature [Ancius et al., 2005; Dragusin, 2006].

The radionuclide specific activity inventory of the irradiated graphite from the thermal column of the VVR-S Reactor is presented in Table 3 (main radionuclides). – (Samples D2.1, D3.1, D4.1, D5.1, D6.1-1 collected from a location nearer to the reactor core and samples D1.2, D2.2, D3.2, D4.2, D5.2, D6.2-2 collected from the location opposite to the reactor core).

Table 3: Radionuclide specific activity in graphite samples collected from VVR-S Reactor thermal column

Graphite sample	^{14}C [Bq/g]	^{60}Co [Bq/g]	^{154}Eu [Bq/g]
D6.1-1	3.4 E+4	3.4 E+3	1.3 E+3
D6.2-2	2.6 E+3	2.6 E+2	3.3 E+1
D5.1	20	2.0	1.6
D5.2	4	0.4	0.37
D4.1	---	<MDA	<MDA
D4.2	---	<MDA	<MDA
D3.1	---	<MDA	<MDA
D3.2	---	<MDA	<MDA
D2.1	---	<MDA	<MDA
D2.2	---	<MDA	<MDA
D1.2	---	<MDA	<MDA

MDA=Minimum Detectable Activity

The result of the specific activity estimation for the key radionuclide ^{60}Co in the thermal column has been validated by dose rate measurements. The contributions to the dose rate of other radionuclides, like ^{154}Eu and ^{152}Eu , have been neglected because they are smaller than 5%.

2.3 Accelerator Mass Spectrometry based on the 9 MV and 1 MV accelerators of IFIN-HH for measurements of ^{14}C concentration in irradiated graphite

2.3.1. Introduction

Accelerator Mass Spectrometry (AMS) is a very unique and special method of selecting and counting atoms of a certain kind individually. It has the highest analysis sensitivity known today: 10^{-16} (ratio: isotope/element). By use of reference samples it provides quantitative results expressed in suitable units (Bq/g, atoms/cm³, atoms/l etc.) which have certain advantages compared to other employed methods.

The history of invention of this method goes back at the end of the 1960's when the new atomic analyzing method was born from the desire of separating a new light isotope, ^3He . The basic idea was to try to separate two isobars (^3H and ^3He) by taking advantage of the differences between charge states, if the ions were to completely lose their electrons (1^+ and 2^+). It was rapidly recognized that such a charge separation, and also the separation of ion masses in general, will be stronger if the ions have a higher energy that can be gained by using a particle accelerator. In this

way, the Accelerator Mass Spectrometry (AMS) was invented and the Nobel Prize was awarded to L.W. Alvarez and R. Conrog for the related discovery of tritium (Alvarez & Conrog, 1939).

The long-lived radionuclides are analysed by AMS, free of molecular interference, and with the detector background at isotopic ratio as low as 10^{-16} . This is the equivalent of having the possibility to select and register one single type of atom from a million of billions of other types of atoms. Today, after about 50 years of development, the applications of AMS nanotechnology are leading researches in many areas of our science and of everyday life.

2.3.2. AMS General Description

AMS measures isotopes concentration in a sample material in solid state. The sample material has to be transformed into a confined ion beam, with good emittance, so that it can be transported on a long path through a particle accelerator and through many analyzers.

A typical AMS facility, as presented in Figure 7, consists of four major parts: the ion injector (containing the ion source), the tandem accelerator; the high energy analyzing systems and the particle discrimination and detection system.

The sample should be of solid substance with good thermal and electrical conductivity. In the ion source, an accelerated beam of positive ions of ^{133}Cs is accelerated and focused to bombard the sample. By this sputtering process all kinds of atoms will be scattered out. However, only the negative ions will be extracted from the ion source, since they are only ions accepted at the entrance of the linear tandem accelerator. The ion source avoiding neutrals and positive ions and molecules represents a first filter for the analyzer (F1).

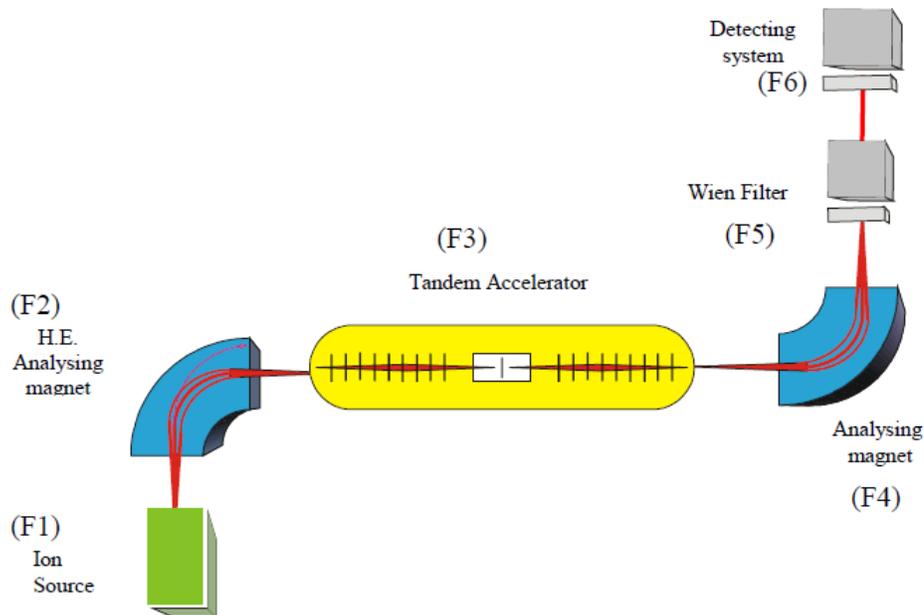


Figure 7: Schematic diagram of an AMS- facility

A second filter is the 90° double focusing analysing magnet (F2). The negative ions with charge state 1^- will pass through this magnet and will be selected according to their mass value with a resolution of $\Delta m/m=1/250$. Then, before entering into the tandem accelerator, the selected ions species will be further accelerated up to about 70 keV. This energy increase is necessary to reduce the source emittance and in order to match the entrance acceptance of the tandem accelerator. At the central terminal position, the accelerated ions have to pass through the stripper foil (carbon foil or gaseous medium) and lose part of their exterior electrons by a stripping process in the foil. In this way, the negative ions will change to positive charge, with different values according to their energy ($q = 2^+, 3^+, 4^+, 5^+, 6^+, 7^+, \dots$). Molecules passing through the terminal stripping foil are fragmented and removed from the ion beam. That is the reason why the stripper foil is considered to be a third filter (F3). The now positively charged ions will be repelled by the positive high voltage terminal. They will be accelerated in the second half of the tandem accelerator system, down to the ground potential at the exit of the tandem accelerator. A powerful magnetic analyzer then performs a mass separation of high resolution. This is the fourth filter (F4). Since the magnetic field cannot separate particles with the same p/q ratio (ratio momentum/charge), a Wien velocity filter or an Electric Filter (Electrostatic Analyzer, ESA) can be used to separate ions according to their velocity and in this way remove the magnetic degeneracy. The filter is located in between the HE analysing magnet and the detection system. This is the fifth filter (F5).

Finally, the AMS facility ends with the particle detection system. This is the last filter (F6) and performs mass and isobar separation. AMS is usually a relative analyzing method and requires standard samples. In this way it delivers the absolute values of the measured concentrations.

The goal of the present research study is to measure ^{14}C accumulations and possible contaminations in nuclear materials from the VVR-S reactor in IFIN HH. The ^{14}C has a half-life of 5370 years. It is produced in the Earth's atmosphere and in the nuclear reactors by the reaction of high energetic neutrons with nitrogen. ^{14}C concentrations in different materials and components of the reactor may vary on a large scale with distance from reactor core and also, may depend on the depth in a sample from a particular location. Therefore, in this project and depending on the expected concentrations of ^{14}C , two different AMS facilities are used, as follows:

- 1) The AMS facility of the 9 MV tandem accelerator:
 - for ^{14}C exceeding the current natural level of 10^{-12} in relation to the current natural ratio of $^{14}\text{C}/^{12}\text{C}$ and for performing the depth profiling of the concentration in materials.
- 2) The AMS facility at 1 MV tandetron :
 - for ^{14}C concentrations below the current natural level of 10^{-12} in relation to the current natural ratio of $^{14}\text{C}/^{12}\text{C}$.

The AMS facility at 9 MV tandem accelerator is shown schematically in Figure 7 and photos of the injector and the accelerator are presented in Figure 8a, below.



Figure 8a: Left: the Injector deck of the 9 MV tandem AMS facility in Bucharest: (1) Injector platform polarized at -100 kV, (2) second platform polarized at -30kV in respect to the first platform, (3) the ion source (40 NC-SNICS), (4) 90° analyzing magnet, (5) slits and retractable Faraday cup, (6) pre-acceleration NEC tubes. Right: the tandem 9 MV FN accelerator.

The second AMS facility, devoted to hyper-sensitive analyses is presented in Figure 8b:

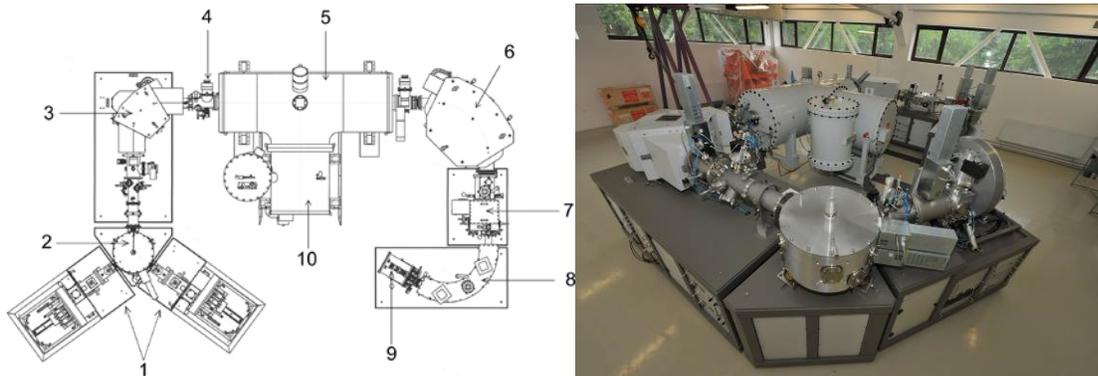


Figure 8b: Left: the general layout of 1 MV HVEE AMS facility in Bucharest, Romania. Right: photograph of the facility.

(1) Two ion beam injectors equipped with SNICS ion sources of type SO110 – 50 sample carousel HVEE and focusing ion lenses; (2) electrostatic switching system; (3) injection Magnet with multi beam switcher (bouncer); (4) Faraday cup and Q-Snout device; (5) 1 MV tandetron accelerator, with gas stripper channel; (6) analyzing Magnet; (7) three offset Faraday cups; (8) electrostatic analyzer; (9) particle detector; (10) Cockcroft–Walton type HV power supply.

3 Experimental Results

3.1 Determination of ^{14}C in virgin nuclear graphite samples with low concentration.

As presented in the previous section, such measurements are performed with the 1 MV AMS facility in IFIN-HH. The machinery was purchased from the HVEE company and is completely computer controlled (Stan-Sion et al. (2014) and Stan-Sion et al. (2015)).[4][5]

The samples of ^{14}C were cut from virgin nuclear grade graphite as used in the subcritical assembly *Helen* and by the Russian nuclear reactor of VVR-S type. About 20 mg of material of virgin graphite, transformed to powder, was loaded and pressed into 8 sample holders of the ion source, together with reference and blank carbon samples. Each sample was counted 3 times for 5 minutes in a process divided into 10 blocks of 30 seconds counting. The total number of ^{14}C for 15 minutes was approximately 25000 counts, thus the statistical error was 0.6%. For reference samples and background samples this error was 0.3% and 0.8%, respectively. All results were corrected for the background value and calibrated according to the reference samples. Figure 9 presents the bi-parametric spectrum of the reactor graphite sample measured during one of the runs performed (lower figure), as well as the bi-parametric spectrum of the standard sample (upper figure).

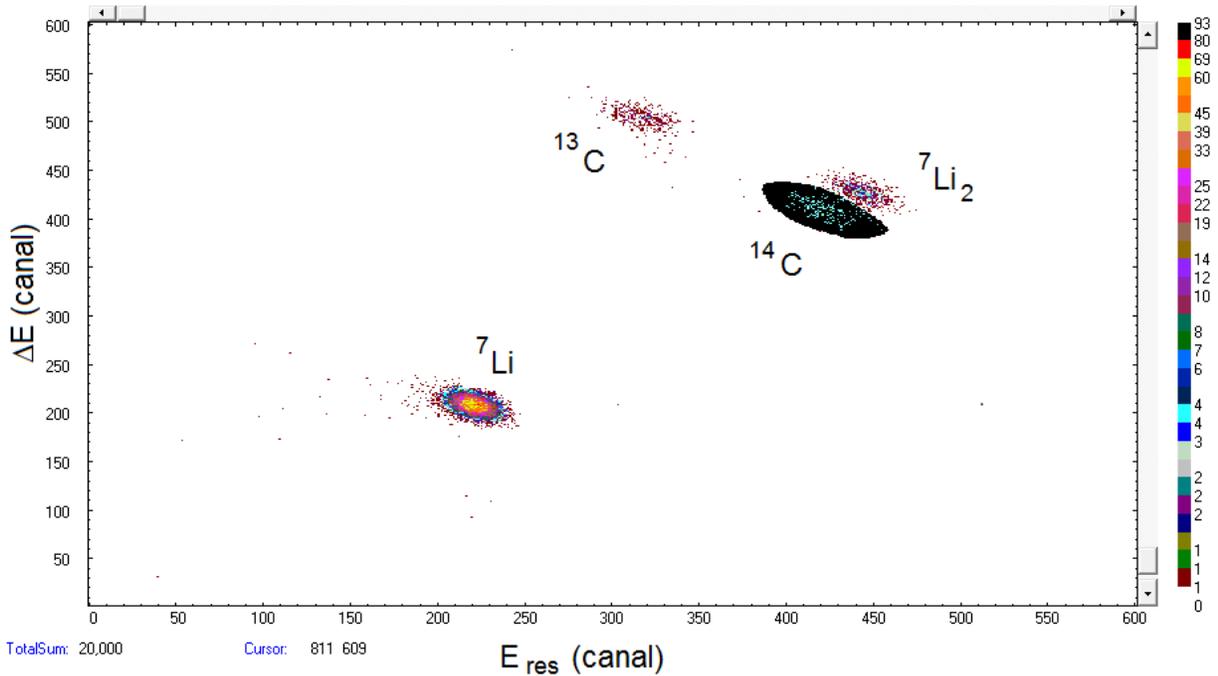
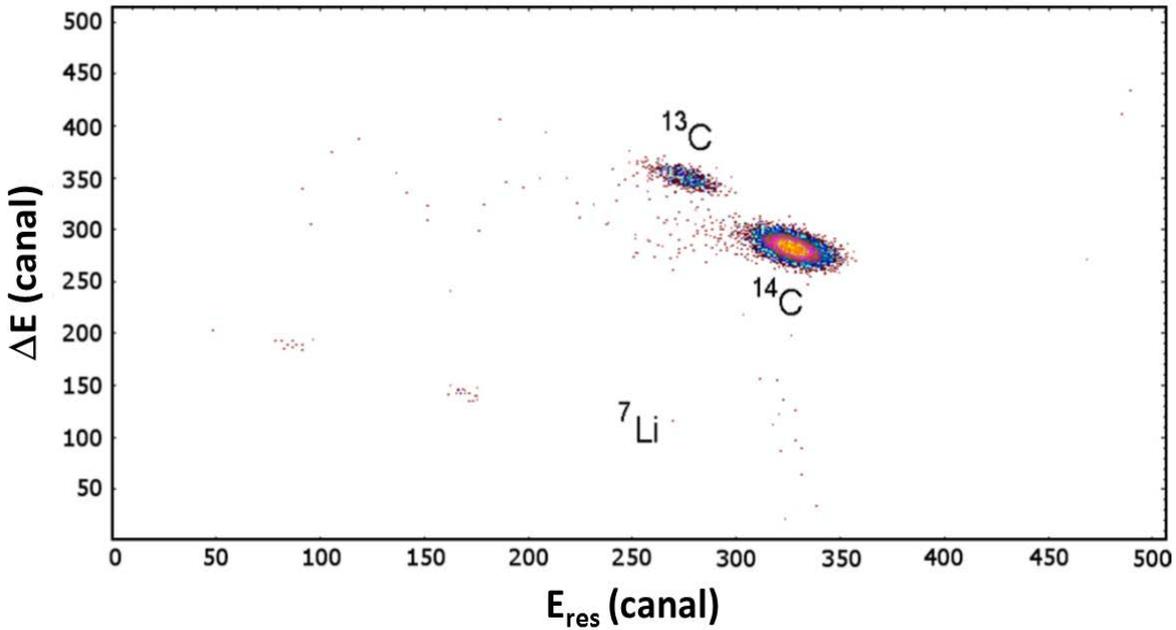


Figure 9: Two bi-parametric spectra showing the ^{14}C concentration.

The spectra represent the standard sample and reactor sample. The lower spectra are the measurement of the reactor sample and contain $^7\text{Li}_2$, which is an interfering molecule of mass 14 that is partially broken in the two fragments when it enters into the gas field detector. However,

the unbroken part of the molecule contributes with its energy release to the upper part of the ^{14}C counting region and affects the recorded data of the true concentration. It will be removed by choosing a gate (black spot), free of Li content.

Figure 10 and Table 4 present the results of measurements of ^{14}C in two unirradiated graphite samples of the same types as used in subcritical assembly *Helen* and VVR-S reactor. Samples were collected from the surface (surf.) and from the interior (int.) of the virgin graphite rods.

In spite of the fact that all measured samples are cut from virgin graphite of non-exposed rods, the concentrations are 2 orders higher on the surface compared the bulk value (see Table 4). A possible explanation is the contact of the exterior surface with the atmosphere.

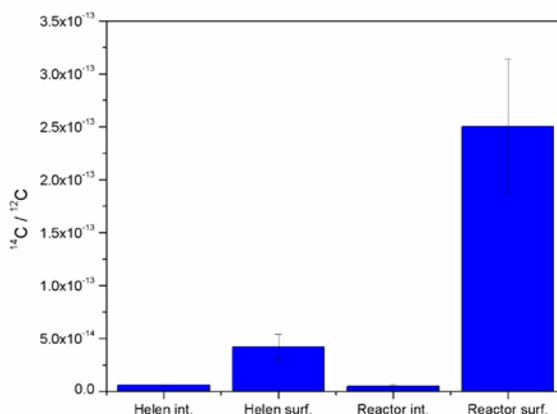


Figure 10: The ^{14}C concentrations measured from samples of unirradiated graphite as used in the subcritical assembly *Helen* and the VVR-S reactor

Table 4: AMS-measured $^{14}\text{C}/^{12}\text{C}$ ratios for irradiated graphite samples

Sample	$^{14}\text{C}/^{12}\text{C}$ ratio	
	Average value	Standard deviation
Helen interior	6.08E-15	5.01E-16
Helen surface	4.22E-14	1.21E-14
Reactor interior	5.02E-15	1.5E-15
Reactor surface	2.5E-13	6.35E-14

3.2 Determination of ^{14}C in graphite samples collected from graphite column of the VVR-S reactor using AMS 1 MV facility

The first measurements at 1 MV AMS machine were performed on samples collected from disc number 2. The samples of graphite were cut from disc number 2 of the graphite column – 3 samples were collected from inside and outside the graphite coating of the rod’s edge nearer to the reactor vessel (**Samples 2.1**) and the other 3 samples from the opposite part of the graphite coating the rod (**Sample 2.2**). About 20 mg of material of the samples (from both face of the samples) were transformed to powder and loaded and pressed into 8 sample holders_(2 mg/sample)-of the ion source, together with reference and blank carbon samples (reference sample HOxII: 18.40 dpm/g (0.31Bq/g)).

Each sample was counted 3 times for 5 minutes.

The results of the 3 set of measurements are presented in Figure 11.

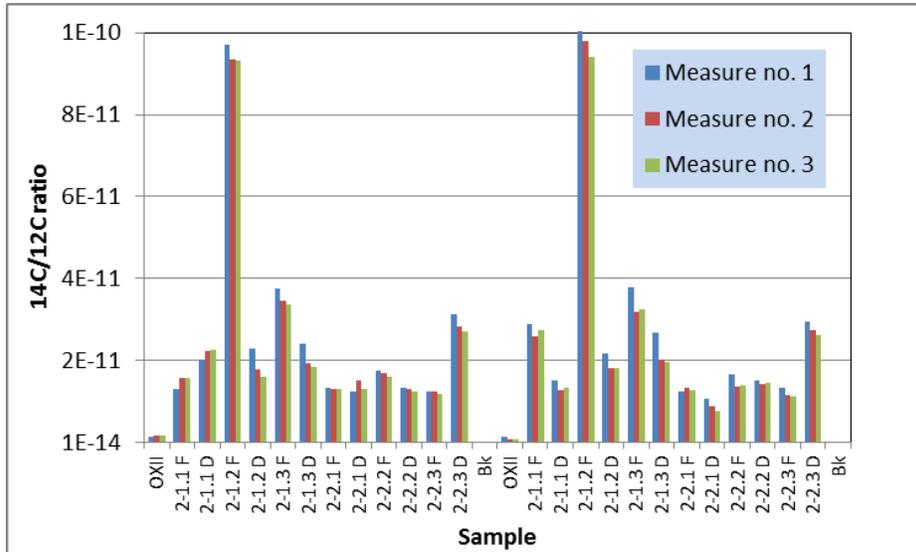


Figure 11: The $^{14}\text{C}/^{12}\text{C}$ ratio measured from samples collected from graphite disc number 2 (Bk=Blank; OXII=Standard 18.40 dpm/g (0.31Bq/g); 2.1, 2.2, etc. =Samples; F,D=Sample's face; 1,2,3=No of the samples)

The ^{14}C concentration (Bq/g), calculated as the average of 3 measurements in samples 2-1 and 2-2 from the graphite disc are presented in Figure 12:

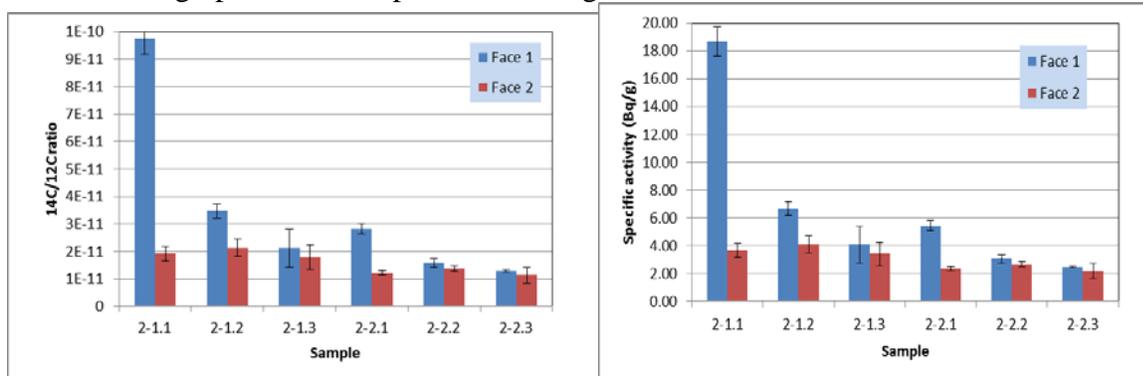


Figure 12: The $^{14}\text{C}/^{12}\text{C}$ ratio and specific activity measured from samples collected from graphite disc number 2.

As can be observed, the result from one of the samples (sample 2.1.1, face 1) is about 3 times higher than the other face of the same sample, probably due to a cross contamination. This value was excluded from the final calculation of the ^{14}C specific activity, which is noted as follows for Samples 2-1 and 2-2:

- Sample 2.1 (disc number2-graphite column) = 3.73 ± 0.36 Bq/g
- Sample 2.2 (disc number2-graphite column) = 2.39 ± 0.24 Bq/g

The results are in agreement with the fact that sample 2.1 was collected from the end of the rod nearer to the reactor core.

Due to the high concentration of ^{14}C , samples collected from the discs 5 and 6 were diluted 100 times using ultrapure graphite ($^{14}\text{C}/^{12}\text{C}$ atoms ratio = $6\text{E}-15$; sourced at Alfa Aesar Johnson Matthey GmbH, Germany). Since the two powders that were to be mixed had different grain sizes, dilution was made using a mortar agate in which 1 ml ultrapure water was added. About 20 mg of the mixed powder was pressed into the sample holders.

To ensure optimum measurement (provided by a given current source sufficiently large), all samples (diluted or undiluted) were mixed in a mass ratio of 1:5 with Metals (^{14}C free; sourced at Alfa Aesar Johnson Matthey GmbH, Germany). The mixture obtained was loaded into holders of the ion source and measured.

The AMS experiments were performed on samples collected from these locations and results are shown in Figure 13. Precise standard samples were used to determine the radiocarbon concentrations.

The graphite's samples were collected from the inner and the outer surface of the graphite sleeve of the rod's edge near to the reactor vessel for the column discs no 1-4, (**Sample code: D2.1, D3.1, D4.1**) and the others from the opposite part (**Sample code: D1.2, D2.2, D3.2, D4.2**). The sample codes collected from graphite rods from column disc 5 and 6 have been mentioned before: D5.1, D6.1-1, D6.1-2 and D5.2, 6.1-2, 6.2-2 (see also Figure 5). Figure 14 shows the evolution of the standard samples at the beginning and at the end of the experiment. The increases in outspreading and statistic fluctuations are due to the high concentration of samples that produced a memory effect on the analyzing system.

The same memory effect for samples with high concentration is revealed also by the increase of the background, as shown Figure 15.

Unfortunately, radiocarbon concentration for disc 6 (sample 6.1) could not be measured, due to limitation of the 1MV AMS machine to concentrations exceeding the natural level of radiocarbon. These samples will be re-measured at the AMS facility by 9 MV accelerators that possess calibrated beam attenuators and are able to measure higher concentrations (by about a factor of $1\text{E}3$). Note that results from sample 6.2, even though they are presented in Figure 13,

are unreliable; these samples will also be re-measured at the AMS facility, also by 9MV accelerators.

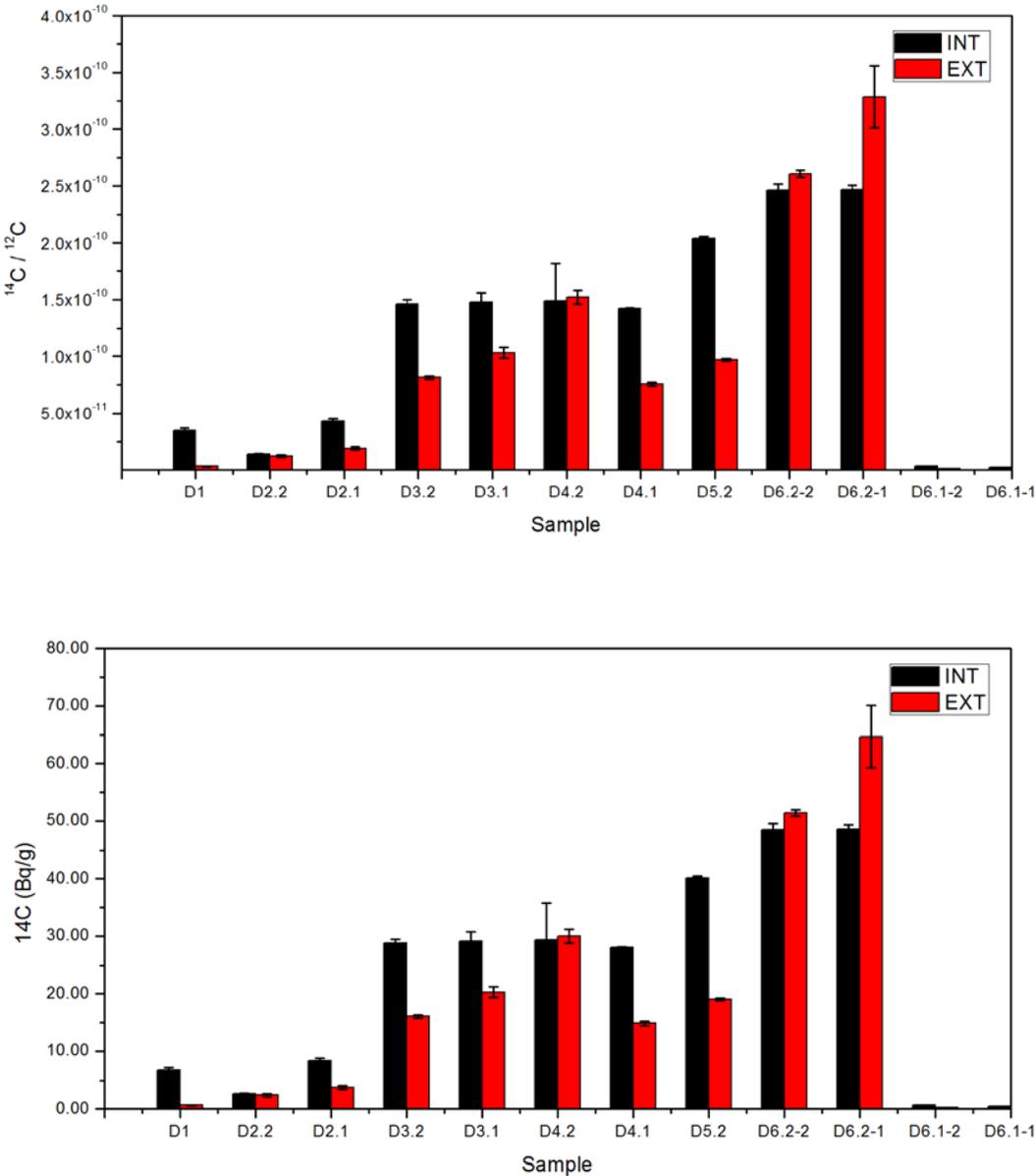


Figure 13: Results of the AMS experiments determining the ^{14}C concentration accumulated in the thermal column of the VVR-S reactor

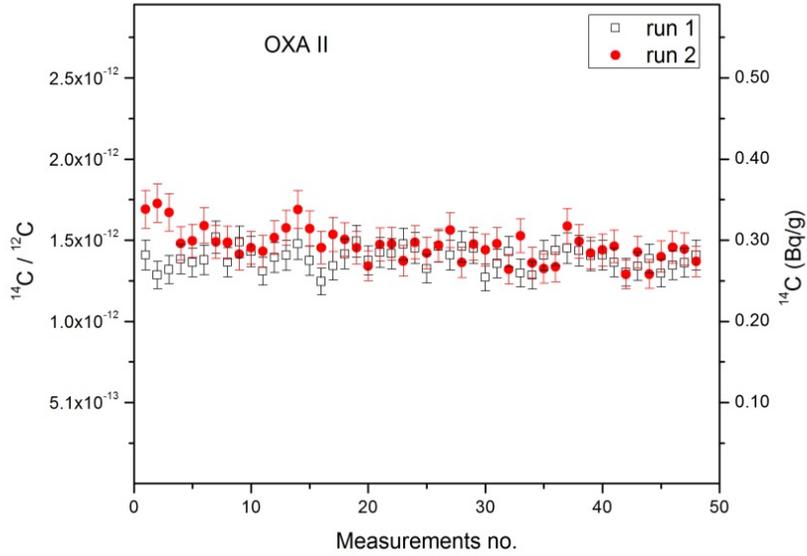


Figure 14: AMS results of the standard sample (OXA II) used in this experiment

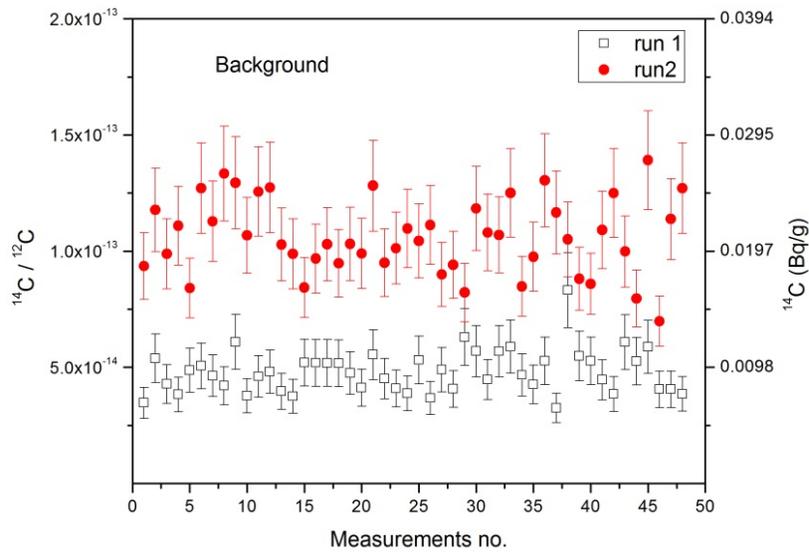


Figure 15: Background radiocarbon concentration measured from blank samples

Figure 15 shows the evident memory effect introduced by the high concentrated samples from the reactor. With the calibrated beam attenuators and with the use of the new high speed and low noise Preamplifier ORTEC 142A (recently purchased in the frame of this project), the next AMS measurements will provide the missing information. However, the new Preamplifier was used also in the present experiment, improving the energy resolution and frequency of event counting.

The numerical results of the AMS measurements are listed in Table 5.

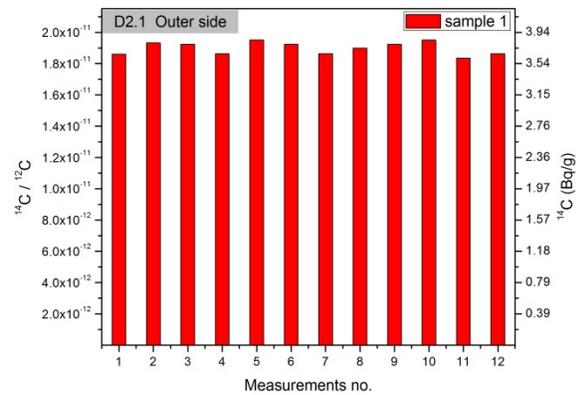
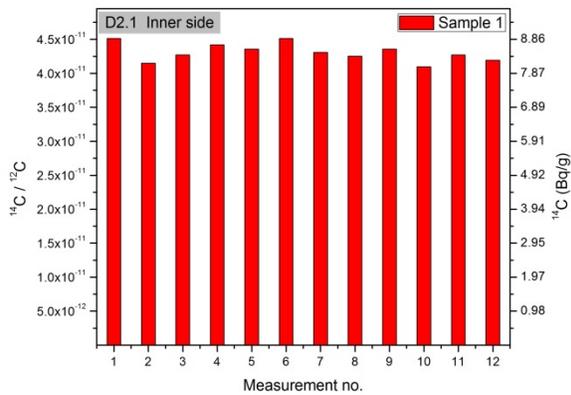
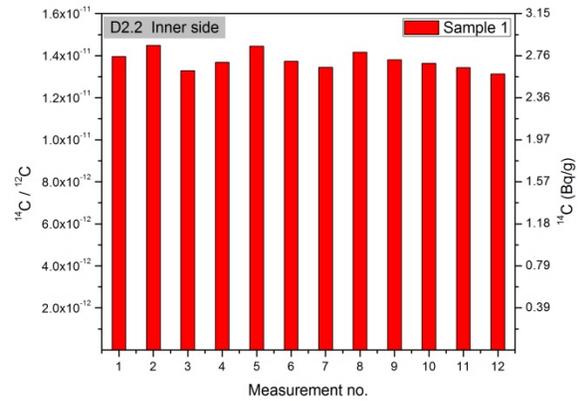
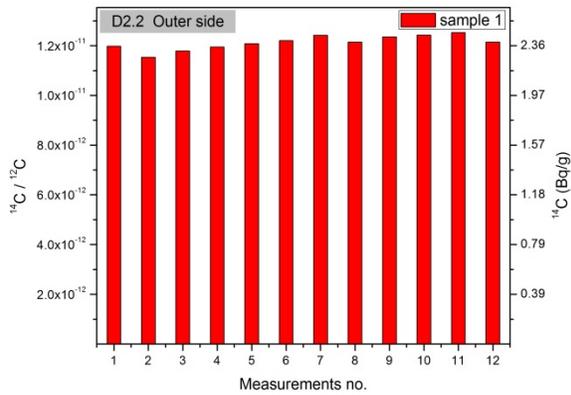
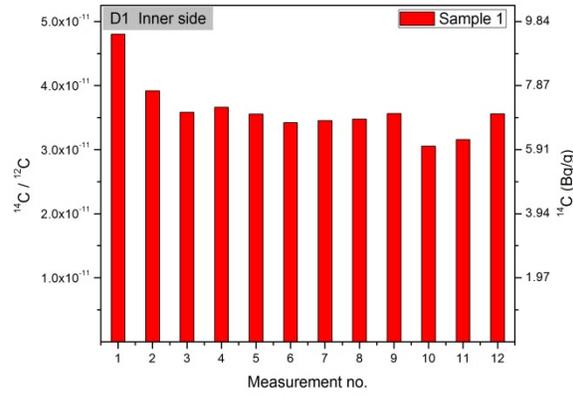
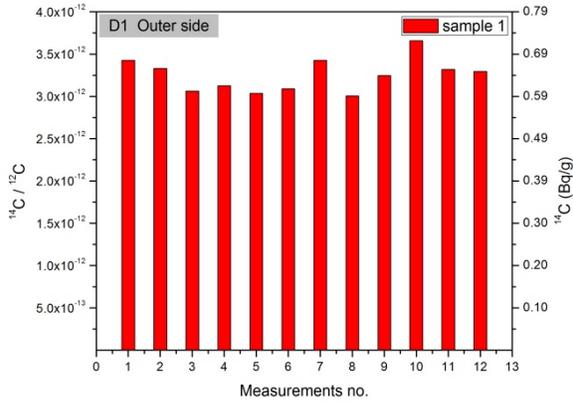
Table 5: ^{14}C concentration in graphite samples

Sample	Outer side		Inner side		Weighted Average $(x_{avg} = \frac{\sum_{i=1}^N x_i w_i}{\sum_{i=1}^N w_i};$ $\sigma_{avg} = \frac{1}{\sum_{i=1}^N w_i})$
D1.2	0.64	0.04	6.85	0.45	0.69 ± 0.04
D2.2	2.39	0.24	2.71	0.08	2.68 ± 0.08
D2.1	3.73	0.3	8.48	0.43	5.29 ± 0.25
D3.2	16.04	0.27	28.74	0.72	17.56 ± 0.25
D3.1	20.28	0.95	29.13	1.61	22.55 ± 0.82
D4.2	29.92	0.37	29.33	6.42	29.92 ± 0.37
D4.1	14.88	0.22	27.95	0.13	24.67 ± 0.11
D5.2	19.07	0.59	40.16	0.31	35.69 ± 0.27
D5.1	Not	measured	Not	measured	
D6.2-2	51.38	5.37	48.43	1.06	48.54 ± 1.04
D6.2-1	64.76	0.02	48.62	0.72	64.74 ± 0.02
D6.1-2	Not	able	to	measure	
D6.1-1	Not	able	to	measure	

Figure 16 (below) shows the statistical accuracy and errors for the different runs during the AMS measurements for both sides of the cylindrical graphite cover. Figures with red and black bulks represent two different measurements for a sample from the same location.

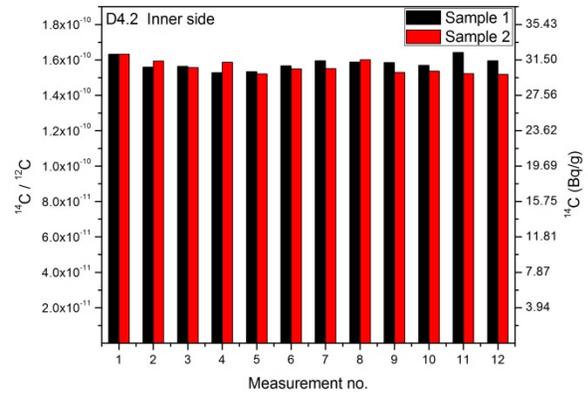
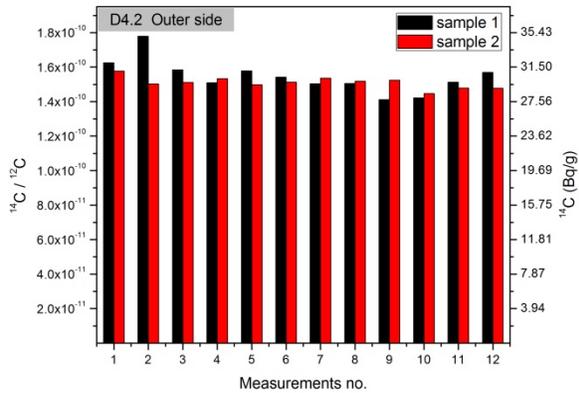
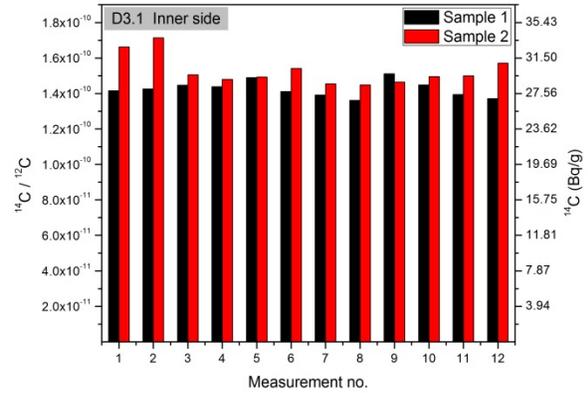
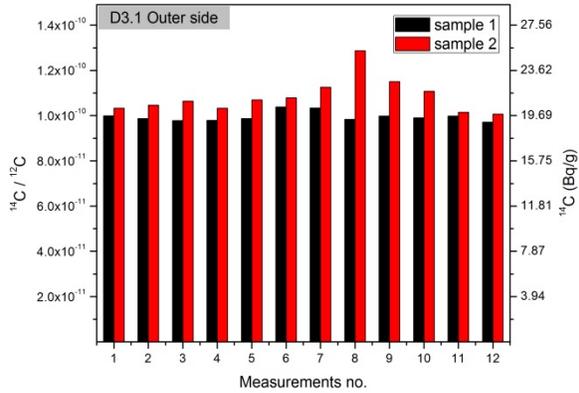
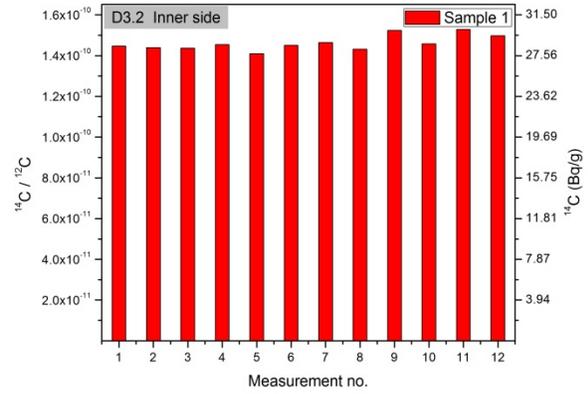
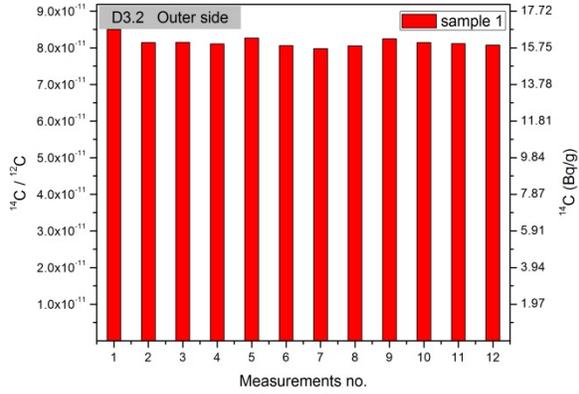


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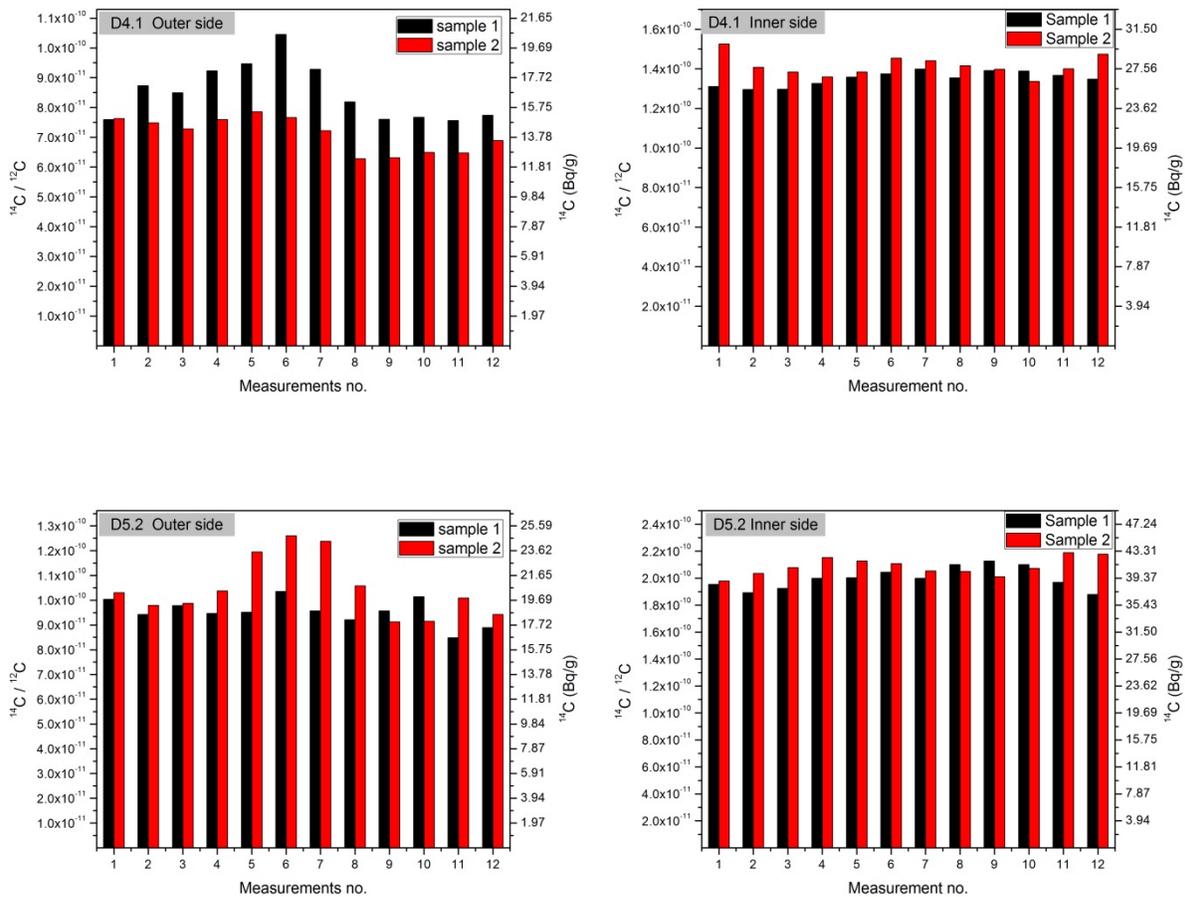


Figure 16: Statistics of AMS measurement for the analyzed samples (results for sample 6-2 are not shown, as they are unreliable).

For high concentration (samples collected from disc numbers 5 and 6) of ^{14}C the deviations are very large and such results are subject for a new experiment adequate to higher radiocarbon concentrations (9 MV AMS facility).

3.3 AMS determination of ^{14}C in graphite samples of high radiocarbon concentrations collected from graphite column of the VVR-S.

For measurement of high concentrations of radiocarbon samples and to provide the depth profile of the evolution of these concentrations towards the bulk, we used the AMS Depth profiling facility at the 9 MV tandem accelerator.

Since depth profiling is requiring a specialized ion source and special prepared acquisition we took advantage of the upgraded work performed at this machinery. A detailed description is given in Stan-Sion et al. (2014) and Stan-Sion et al. (2015).

Regarding the AMS measurement, since ^{14}C measurement implies the elimination of molecular interferences on the high energy side of the accelerator a velocity filter (Wien Filter) is a good the solution. Many interferences occur during ^{14}C measurements like $^{12}\text{CH}_2$, ^{13}CH , $^7\text{Li}_2$, ^{14}N etc. The elimination or reduction of these interferences was the major task of these measurements at this stage of the project, since the AMS facility at the 9 MV accelerator is not designed for such special analyses as are the dedicated ^{14}C machines today.

In our test experiments, we have been using the ^{13}C ion beam for tuning that is about 100 times less intense than the ^{12}C ion beam and therefore more suitable for the adjustment of the beam transport and adjusting the values on the Wien Filter. Higher currents will produce the breakdown of the high voltage on the deviation plates of the Filter.

The optimum value of the magnetic field of the Wien Filter has been determined by tuning it accordingly to a maximum current in a Faraday cup, by keeping the value of the electric field set to a constant value of 14 kV. The magnetic field values for ^{14}C were then calculated and set blindly. To optimize the Wien Filter setting a scanning of different magnetic field values was done according to the obtained data drawn in Figure 17.

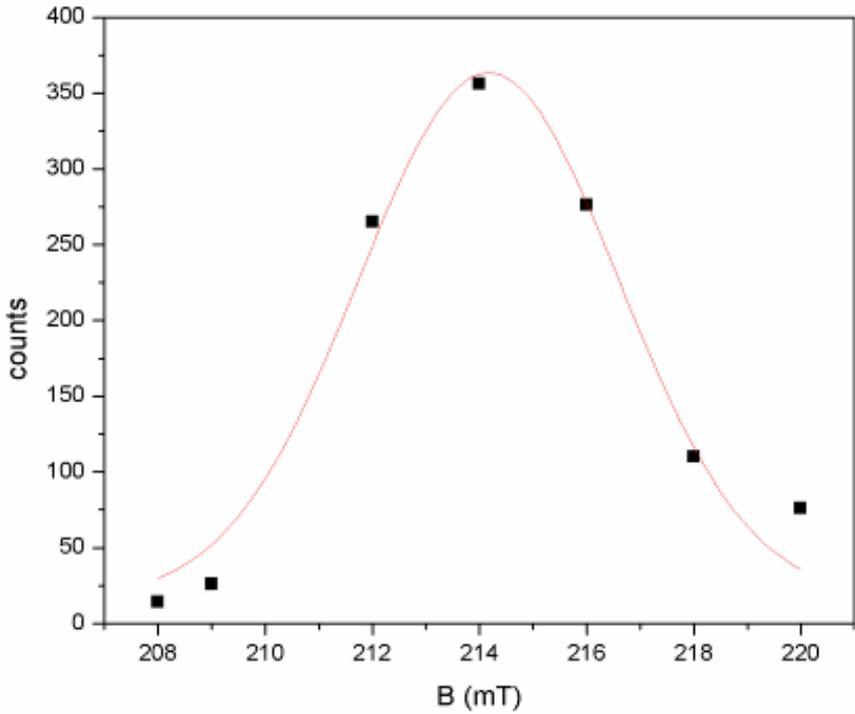


Figure 17: Determination of the optimum magnetic field setting for the Wien Filter

The obtained results are shown in Figure 18; the upper spectrum represents the measured ¹⁴C concentration without a Wien Filter. Molecular interferences are hiding the ¹⁴C peak. The lower spectrum is showing how the Wien Filter is eliminating many of the interferences and ¹⁴C can be distinguished.

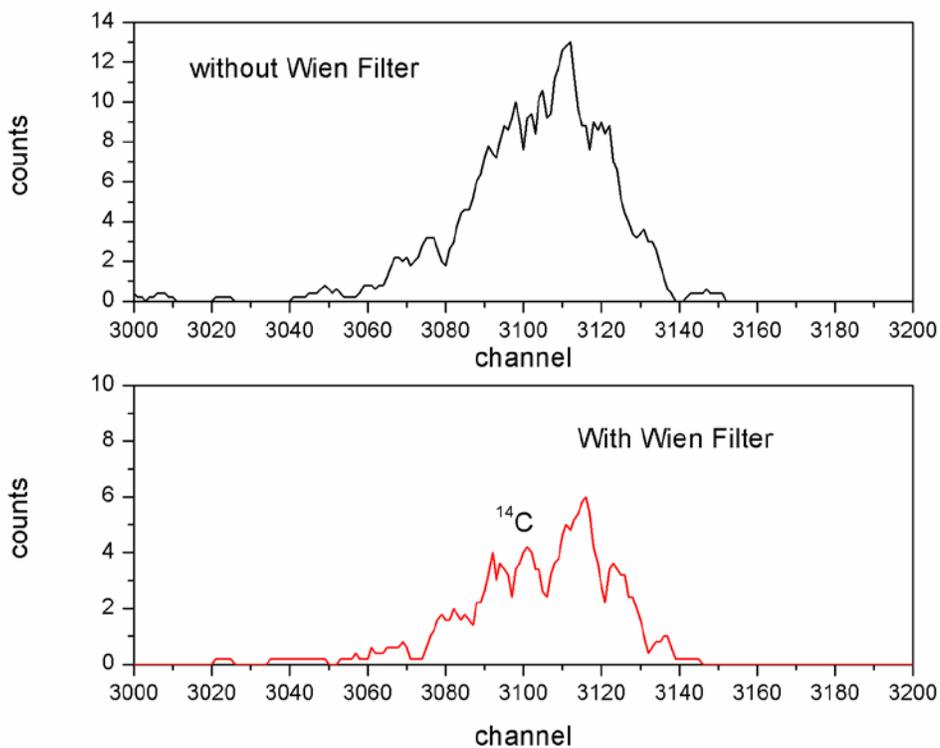


Figure 18: ^{14}C spectra at the 9 MV tandem accelerator.

Figure 18 shows how the interference ions and molecules are contributing to the ^{14}C peak, since energies are very close. A better separation of the ions of different energies can be obtained if the produced signal in the detector is well adapted as input signal to the Spectroscopic Amplifier by a high resolution and time-rapid Preamplifier with low background contribution. This matches the impedances between the two electronic devices and preserves the energetic separation of the detector.

In this respect the performed experiments have shown that replacing the actual Preamplifier is compulsory. Therefore, we purchased from ORTEC Company a preamplifier model 142A PA – ORTEC that provides a maximum noise level of 3.4 keV at 100 pF and a resolution of 50 keV at 5 MeV. The Model 142A is optimized for extremely low noise and fast timing for detectors with capacitance up to 100 pF. This makes it the ideal selection for high-resolution alpha- and beta-particle spectroscopy applications.

The new ORTEC preamplifier was connected to the electronic detection system and preliminary tests have been performed, in order to measure the maximum noise level, charge sensitivity and

stability using one of the barrier layer detectors (silicon surface barrier detector) ORTEC data acquisition chain. The amount of noise (noise width) obtained was 7.9 keV and sensitivity to load (charge sensitivity) obtained was 47 mV/MeV

The relative intensity of the ^{14}C signal to the signals of the other participating ions or molecule also contributes to a better separation of the envisaged ion element. Unfortunately, the ^{14}C current intensity was weak due to the malfunctioning of the pre-accelerating tube (NEC) in the existing conditions. This was because the distance, from the exit of low energy 90° magnetic analyzer to the entrance into the pre-acceleration stage, was too short and the ^{12}C beam was permanently spread out into the acceleration tube producing its electric breakdown. This problem was recently solved by introducing an ion beam aperture defining the ion beam and avoiding lateral out-spreading. This change of the low energy beam line will make it definitely possible to perform measurements without interferences from any neighbouring ion, improving the overall ^{14}C beam intensity and contributing to a better resolution for the analysis of ^{14}C in conditions of depth profiling measurements.

3.4 The determination of ^{14}C surface activity in the graphite samples collected from the thermal column of the VVR-S reactor.

Initially, the ^{14}C surface distribution was planned to be measured using the Beta Imager device. Due to the failure of an electric valve, the Beta Imager was not working properly and the measurements of i-graphite could not be performed.

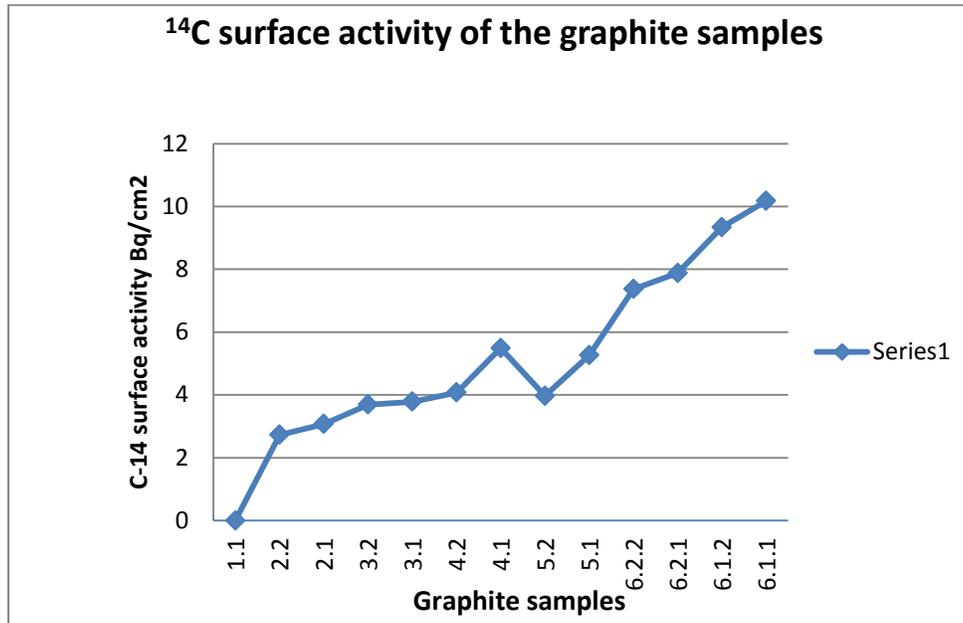
In order to characterize the ^{14}C surface activity of the graphite samples a radioactivity TLC analyser was used. Small discs (10 mm diameter and 2 mm thick) have been cut from each sample collected from the graphite discs of the thermal column of the VVR-S Reactor. The discs have been measured using a radioactivity TLC analyser RITA (Radioactivity Detector for Thin-Layer-Chromatography-Ray test manufacturer) was used to determine the variation of the surface activity of ^{14}C along the thermal column axis.

RITA uses a linear analyser detector (gas flow proportional), which is sensitive over the entire chromatogram trace from the start to the front. The entrance window can be open for ^3H -applications or closed for ^{14}C or any other beta- or beta+ radiation emitting nuclides. Counting gas is a non-inflammable mixture of 90% argon and 10% methane, which is traded as P10 gas. RITA can operate with very high sensitivity in open window detection mode for ^3H measurement or closed window detection mode for ^{14}C , ^{18}F , ^{11}C etc. The sensitivity for is ^{14}C count of 1.6 Bq in 10 minutes.

The experimental results of the RITA measurements are presented in Figure 19 (the graphical representation of the results on a logarithm scale are presented) and the surface activity of ^{14}C in graphite samples are listed in Table 6.

Table 6: ^{14}C surface activity of the graphite samples collected from thermal column of the VVR-S reactor

SAMPLE	^{14}C SURFACE ACTIVITY (Bq/cm ²)
1.2	Background
2.2	15.29
2.1	21.66
3.2	40.05
3.1	44.03
4.2	59.00
4.1	242.04
5.2	53.04
5.1	192.82
6.2-2	1585.72
6.2-1	2640.39
6.1-2	11403.18
6.1-1	26309.64

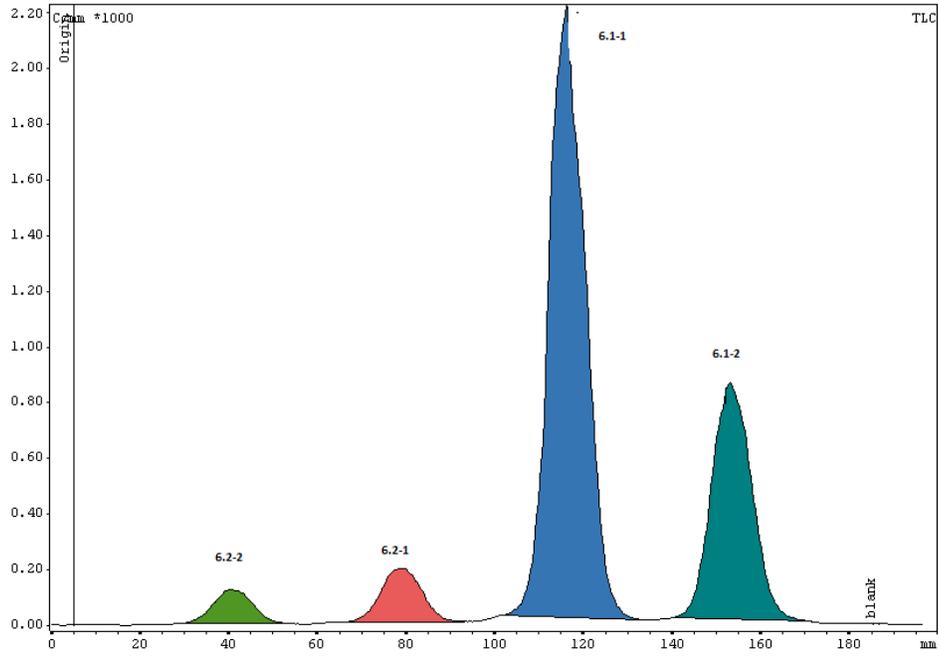




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Integration C:\GINA_Star_TLC\2016\VF\GRAFIT_P6GLOBAL, Grafit_p6global.rta



Sample description

Study: 2016
Measurement: Grafit_p6global.rta, started 2/24/2016 10:07AM
Method: : VF
Origin: 0:05:00 Resolution: 0.33mm Energy: 30-750keV
Meas. time:
Traynumber: 1
REACTOR GRAPHITE SAMPLE DISC 6
Date of device calibration: 12/21/2015 (valid)

Integration TLC

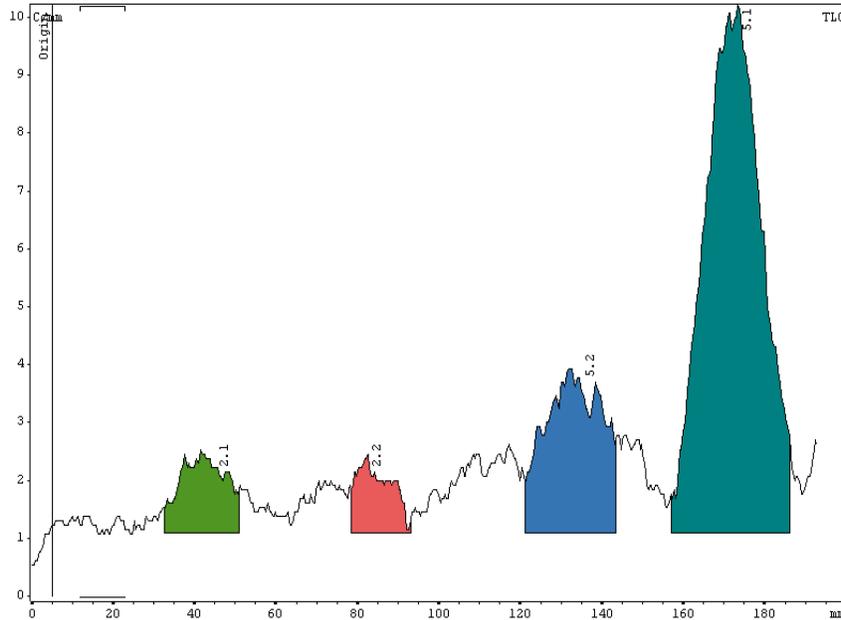
Substance	R/F	%Total %	Type	Area Counts	%Area %
6.2-1.	0.187	3.47	BB(2072.71	3.78
6.2-2.	0.373	5.78	BB(1244.79	6.30
6.1-1.	0.563	57.58	BB(20653.07	62.74
6.1-2.	0.753	24.96	BB(8951.50	27.19
blank	0.925	0.00	BB(-1.00	0.00
Sum in ROI				32921.07	
Total area				35868.00	
Area RF				35860.00	
Ext. BKG				0.00C/mm	



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Integration C:\GINA_Star_TLC\2016\VF\GRAFIT_P2_5GLOBAL, Grafit_p2_5global.rta

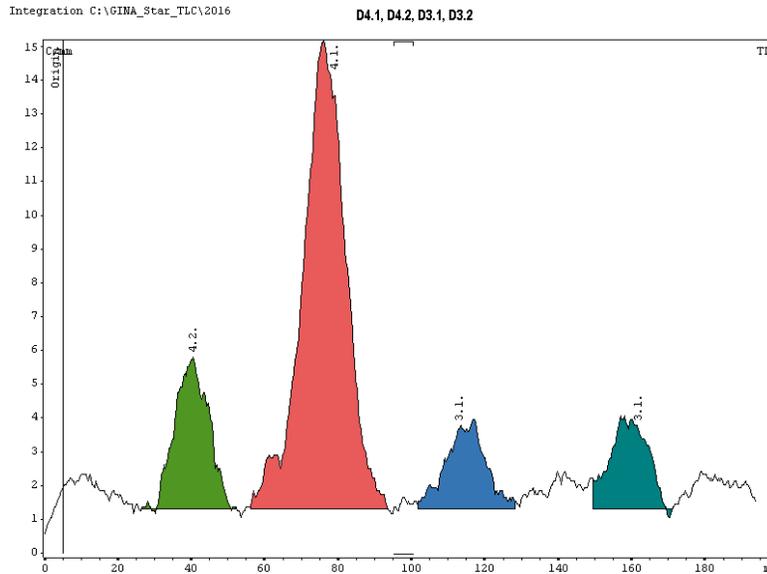


Sample description

Study:	2016		
Measurement	Grafit_p2_5global.rta, started	2/24/2016	10:23AM
: Method:	VF		
Origin:	0:05:00	Resolution: 0.33mm	Energy: 30-750keV
Meas. time:			
Traynumber:	1		
REACTOR GRAPHITESAMPLE: DISC 2 and DISC 5			
Date of device calibration: 12/21/2015 (valid			

Integration TLC

Substance	R/F	%Total %	Type	Area Counts	%Area %
2.1	0.217	5.45	DD(17.0000	7.66
2.2	0.411	3.84	DD(12.0000	5.41
5.2	0.678	13.34	DD(41.6364	18.76
5.1	0.870	48.49	DD(151.3636	68.18
Sum in ROI				222.0000	
Total area				312.1818	
Area RF				312.6364	
BKGL				1.09091	
Remainder RF				90.64	28.99
Remainder(Tot)				90.18	28.89



Sample description

Study:	2016				
Measurement	Grafit_p3_4global.rta, started	2/24/2016	10:23AM		
: Method:	: VF				
Origin:	0:05:00	Resolution: 0.33mm	Energy: 30-750keV		
Meas. time:					
Traynumber:	1				
REACTOR GRAPHITESAMPLE: DISC 3 and DISC 4					
Date of device calibration: 12/21/2015 (valid					

Integration TLC

Substance	R/F	%Total %	Type	Area Counts	%Area %
4.2.	0.183	13.47	DD(46.3125	15.32
4.1.	0.361	55.24	DD(190.0000	62.85
3.1.	0.557	9.14	DD(31.4375	10.40
3.1.	0.805	10.05	DD(34.5625	11.43
Sum in ROI				302.3125	
Total area				343.9375	
Area RF				344.5000	
BKGl				1.31250	
Remainder RF				42.19	12.25
Remainder(Tot)				41.63	12.10

Figure 19: Experimental results of ¹⁴C surface activity distribution along thermal column

4 Conclusions

- 4.1 IFIN-HH developed a method, based on the use of **Accelerator Mass Spectrometry (AMS) based on the 9 MV and 1 MV accelerators** to characterize the distributions of ^{14}C inventory in irradiated graphite from VVR-S Reactor.
- 4.2 Samples extracted from discs 4, 5 and 6 of the thermal column will be re-measured at 9MV tandem accelerator for a more accurate determination of ^{14}C concentration. The measurements will be performed during this year when the beam time at 9 MV tandem accelerator will be assigned.
- 4.3 ^{14}C surface activity of the graphite samples have been measured and the variation of the surface activity along the thermal column of VVR-S reactor has been determined.
- 4.4 All graphite samples will be re-measured using Beta Imager for determination of the surface

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