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**Project no.: PN-III-P1-1.1-PD-2016-0532**
**A fast and reliable method for radiocarbon measurements in air and vegetation**
**Acronym: CARBONMAV**
**Stage 2/31.12.2019:**
**Assessment of the direct absorption method uncertainty and its contribution to the uncertainty budget of the radiocarbon measurements by liquid scintillation method (continuation). Construction and optimization of the $CO_2$ absorption device and of the $CO_2$ purification and bubbling line**

# STAGE 2 REPORT

**Stage 2 Objectives: Assessment of the direct absorption method uncertainty and its contribution to the uncertainty budget of the radiocarbon measurements by liquid scintillation method (continuation). Construction and optimization of the $CO_2$ absorption device and of the $CO_2$ purification and bubbling line**
Activity 2.1: Certify of the direct LSC measurement by AMS measurements;
Activity 2.2: Construction and optimization of a device for the absorption of atmospheric $CO_2$ using static and dynamic conditions into sodium hydroxide solution;
Activity 2.3: Optimization of the bubbling line for direct absorption of $CO_2$ in scintillation cocktail;
Activity 2.4: Management and dissemination.

In the context of climate change, determining the radiocarbon activities in various compartments of the environment is becoming more and more important. Development and testing of thermonuclear weapons in the early 1960s almost doubled the atmospheric content of $^{14}C$ atoms over the level sustained by natural background production rates. Changing production rates presented new opportunities for studying carbon cycling on shorter timescales as compared to the $^{14}C$ half-life. After weapons testing, $^{14}C$ has been used as a global-scale tracer for Earth's carbon cycle. On the other hand, plant materials have proven to be representative for $^{14}CO_2$ at the continental, annual scale, allowing them to be used to understand the spatial distribution of $^{14}CO_2$. Since photosynthetic uptake does not alter $^{14}C$, short-lived annual plants reflect atmospheric $^{14}CO_2$ averaged over their growing season, with the mention that most plants photosynthesize carbon only during the day, and that the magnitude of photosynthetic uptake varies with weather conditions and plant growth phase.

There are three recognized methods for sample preparation applicable to any product that can be turned into $CO_2$ gas. The three test methods are 1) accelerator mass spectrometry (AMS); 2) benzene-LSC; and 3) $CO_2$ cocktail-LSC (direct absorption method). All 3 approaches require the production of $CO_2$ prior to analysis. In the AMS and benzene-LSC methods, the $CO_2$ is converted to graphite and benzene, respectively, and then analyzed by AMS (graphite) and LSC (benzene). AMS and benzene methods are well-known and reliable methods used by many laboratories worldwide, the first technique being very accurate but highly expensive, while the second is very demanding though rather popular. The third approach is based on the same basic principle as the benzene method. The main difference is that the $CO_2$ produced from the sample is directly absorbed into a suitable cocktail with high

$CO_2$ affinity and immediately counted by LSC without any further manipulation. The method is simple, safe, and results in significantly reduced analysis time and cost as compared to the traditional methods.

In the context of climate change, the assessment of the fossil fuel-derived $CO_2$ component from atmosphere is very important. It can be used time-integrated observations of the radiocarbon content of $CO_2$ to quantify the recently added fossil fuel-derived $CO_2$ component at surface sites surrounding a point source. Both fast-growing plant material (grass) and $CO_2$ collected by absorption into sodium hydroxide solution provide excellent time-integrated records of atmospheric $^{14}CO_2$. These time-integrated samples allow the evaluation of emissions over a period of days to weeks with only a modest number of measurements.

In order to reach the general objective of the project, namely the development of a fast and safe method for measuring radiocarbon in air and vegetation by the direct absorption method, the following activities were carried out: i) certify of the direct LSC measurement by AMS measurements; ii) construction and optimization of a device for the absorption of atmospheric $CO_2$ using static and dynamic conditions into sodium hydroxide solution; iii) optimization of the bubbling line for direct absorption of $CO_2$ in scintillation cocktail and iv) management and dissemination.

In the first activity, was organized an intercomparison regarding the determination of C-14 concentration in environmental samples by liquid scintillation (LSC) and accelerator mass spectrometry (AMS). The LSC measurements were performed at ICSI Rm. Valcea, and the AMS measurements by at IFIN-HH. The comparison was made on five environmental samples (thuja leaves, Thuja occidentalis L.) that were collected monthly from April 2019 to August 2019. The results were satisfactory and showed that radiocarbon measurements by LSC provide reliable values although the LSC uncertainties are much higher than that of the AMS measurements. Both methods the sample preparation involves $CO_2$ production, therefore it was performed elemental analysis of the samples. This analysis was performed at ICSI using the THERMO FLASH 2000 analyzer. The elemental analysis involves sample combustion, pyrolysis, and chromatographic separation to determine the concentration of nitrogen, carbon, hydrogen, and sulfur. Since the preparation of the samples for LSC implies the combustion of the dried sample in an oxygen atmosphere, the drying of the samples was done at 60°C until the constant mass. The average humidity was 58.16%, the minimum being 55.9% in April and the maximum 60.9% in August. For radiocarbon measurements by LSC, the minimum value was 102.54 ± 3.69 pMC in June and the maximum value 106.56 ± 3.84 pMC in July. The average radiocarbon activity determined by LSC in this intercomparison was 103.62 ± 3.65 pMC. For the AMS measurements, the minimum value was 101.01 ± 1.01 pMC, and the maximum value was 103.65 ± 1.04 pMC. The mean value of radiocarbon activity determined by AMS was 102.12 ± 1.02 pMC.

The evaluation criterion was based on zeta scores (ζ) as defined by ISO 13528:2015 and acceptability criterion was its values lower than ± 2.

$$\zeta = \frac{A_{AMS} - A_{LSC}}{\sqrt{(U_{AMS}^2 + U_{LSC}^2)}}$$

where: $A_{AMS}$ –AMS radiocarbon activity; $A_{LSC}$ –LSC radiocarbon activity; $U_{AMS}$ –AMS uncertainity, for k=1; $U_{LSC}$ –LSC uncertainity, for k=1.

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The second activity of this stage involved the design, construction, and optimization of a device for the absorption of atmospheric $CO_2$ using static and dynamic conditions into a sodium hydroxide solution. The working hypotheses were the following: the air is sampled with a variable air pump and then passed through a flow meter. or a conventional $^{14}C$ analysis, $CO_2$ from about 25 $m^3$ air is necessary. Therefore, the mean flow rate for a sample integration time of two weeks must be about 75 l/h. After the flow meter, the air passes a gas meter where the amount of the already passed air is monitored. Then the air goes through a wash bottle to get humidified. This prevents the NaOH solution to get too concentrated. Now the air flows through the glass Raschig tube where the $CO_2$ is absorbed by the NaOH in the tube. The tube is slowly rotated with an evaporator drive to renew the absorbing NaOH film on the Raschig rings. The motor acts as a vacuum rotary feedthrough. Based on these aspects, was built a device that allows passive and active absorption of atmospheric $CO_2$ in sodium hydroxide solution. Also, the preliminary procedure for using this device was prepared.

In the third activity, the bubbling line has been optimized for the direct absorption of $CO_2$ in the scintillation cocktail, following the losses due to the evaporation of the volatile compounds from its component. For this purpose, was used a certified material, namely IAEA-C2, Travertine, certified activity of 41.14 ± 0.03 pMC and $\delta^{13}C_{PDB}$ = -8.25 ± 0.31 ‰. The experiments were done by varying bubbling rates. Following these experiments, it was concluded that the optimal flow rate is 0.2 L / min.

For management and dissemination activities in this stage of the project, the following aspects were considered:

- Planning, monitoring, management, and project coordination. Actions were taken to acquire the equipment and materials needed to conduct the experiments from this stage of the project and to prepare the future ones; also, was organized an intercomparison with RoAMS Laboratory;
- Literature study for the design of the experiments necessary to achieve the objectives of this stage;
- In the period 08-14.09.2019 I attended the 5$^{th}$ International Conference on Environmental Radioactivity ENVIRA2019, where was presented the paper „Comparison of two air sampling methods for determination of the radiocarbon level in the atmosphere", authors: Ionut Faurescu, Octavian Duliu, Carmen Varlam, Denisa Faurescu, Irina Vagner, Diana Costinel. The event, which was attended by over 100 specialists from all over the continent, took place in Prague, Czech Republic and was organized by Nuclear Physics Institute of the Czech Academy of Sciences and Czech Technical University in Prague, in cooperation with Comenius University in Bratislava, European Academy of Sciences and Art, International Union of Radioecology and Journal of Environmental Radioactivity;
- Was published the paper entitled "RADIOCARBON LEVEL IN THE ATMOSPHERE OF RAMNICU VALCEA, ROMANIA", authors Ionut Faurescu, Carmen Varlam, Irina Vagner, Denisa Faurescu, Diana Bogdan, Diana Costinel in the RADIOCARBON Journal (IF2018 - 1.531), DOI:10.1017/RDC.2019.146.

**Conclusion:**

**The objectives of the first phase of the project have been met.**