Financing contract no.: PD146 / 2018
Project no.: PN-III-P1-1.1-PD-2016-0532
Fast and reliable method for radiocarbon measurements in air and vegetation
Acronym: CARBONMAV
Stage 1/31.12.2018:
Assessment of the direct absorption method uncertainty and its contribution to the uncertainty budget of the radiocarbon measurements by liquid scintillation method

STAGE 1 REPORT

Stage 1 Objectives: Assessment of the direct absorption method uncertainty and its contribution to the uncertainty budget of the radiocarbon measurements by liquid scintillation method
Activity 1.1: Assessment of losses due to evaporation of volatile compounds of the home-made liquid scintillation cocktail.
Activity 1.2: Determination of the optimum parameters of the sample combustion.
Activity 1.3: Management and documentation

Radiocarbon is present in the environment in small quantities in two main forms: $^{14}CO_2$ present in air or incorporated into organic matter. The balance between these two main forms is maintained due to the carbon cycle. Natural production of ^{14}C occurs in high altitudes of the atmosphere due to interaction of cosmic rays with nitrogen atoms, having an abundance in the atmosphere of about one atom of ^{14}C to 10^{12} atoms of ^{12}C. This ^{14}C is then oxidized into carbon dioxide and then mixed with other atmospheric gases, resulting a steady state of $^{14}CO_2$ in the troposphere where it is then incorporated into vegetation through photosynthesis but also in precipitation and oceans.

In this stage of the project the uncertainty of the direct absorption method and its contribution to the uncertainty budget for the determination of C-14 activity through LSC was evaluated. For this purpose, sources of uncertainty were determined for: sample preparation using the direct absorption method, preparation of sample: scintillation cocktail mixture, radioactivity measurement in the sample, due to the calculation of correction factor of the disintegration and due to the calculation of C-14 activity.

To evaluate the losses due to evaporation of volatile compounds from the scintillation cocktail prepared in the laboratory, experiments were carried out with two samples types with specific activities of C-14 around the natural level. The samples used were ethanol from wine and basil essential oil. The C-14 level in these samples was determined by two methods, namely direct LSC measurement and direct absorption method followed by LSC measurement. By comparing the two methods for samples with different carbon content and low C-14 specific activities, it was possible to optimize the method of direct CO_2 absorption and the evaluation of losses due to evaporation of volatile compounds in the scintillation cocktail. Applying direct measurement method the ^{14}C specific activity obtained from wine ethanol was of 0.231 ± 0.004 Bq g-1 C, the same values being obtained by the measurement of 2, 4, 6, and 8 g of sample, taking into account the uncertainty of the measurement. The ^{14}C specific activity in basil essential oil sample, using the same method, was of 0.233 ± 0.004 Bq g-1 C, confirmed for different sample masses also. Similar values were obtained applying CO_2 absorption method

for 10 min bubbling, for both types of samples. The losses of the volatile components from the home-made scintillation cocktail have been highlighted for 15 and 20 min bubbling, which led to an overestimation of the CO_2 mass detained in liquid scintillation cocktail. The correction factors calculated for wine ethanol were around 0.90 for 15 min bubbling, and 0.88 for 20 min bubbling, similar correction factors being obtained for the basil essential oil sample: 0.92 and 0.89 respectively, despite different carbon content of the studied samples. The ^{14}C measurement method involving CO_2 absorption from combustion gas mixture in 2-methoxy ethylamine (component of the home-made scintillation cocktail), was successfully used to determine ^{14}C from essential oils and natural ethanol. Variation of the bubbling time conducted to the conclusion that, for 10 min bubbling, the ^{14}C specific activity measured in the mentioned samples is similar with the value obtained from direct measurement—a reliable measurement, not involving any kind of sample preparation or quenching on LSC measurement.

A novelty of this project is the use of a scintillation cocktail prepared in the lab. It contains a 2-methoxyethylamine which allows the capture of CO_2 in the form of carbamate. Besides this amine, this type of scintillation cocktail contains two solvents and two fluorescent substances. Due to the constant price increase of the 2-methoxyethylamine, a cheaper alternative was investigated. For this, a series of experiments were designed and performed. In these experiments were used one environmental sample in which the level of radiocarbon was determined using a scintillation cocktail prepared with two types of amines. These experiments involved combustion in the oxygen atmosphere in a Parr 1121 combustion vessel of the sample and control material, and then direct bubbling of the gas mixture obtained in the two scintillation cocktails. In order to evaluate the reproducibility of the method, further experiments were carried out involving the introduction of an additional stage of CO_2 purification by absorbing it from the gas mixture in 5M sodium hydroxide solution. After capture, pure CO_2 was obtained by acidification with 16% hydrochloric acid. Both preparation methods yielded reproducible results regardless of the amine used, 2-methoxyethylamine (MEA) and 3-methoxypropylamine (MPA), respectively. In experiments where pure CO_2 was bubbled, the amount of carbon dioxide captured was higher compared to experiments that involved the direct bubbling of the gas mixture through the scintillation cocktail. The C-14 specific activity values obtained using the cocktail with MEA had an average of 0.296±0.012 Bq/gC for bubbling of the combustion mixture directly from the combustion bomb and of 0.287±0.010 Bq/gC respectively, for bubbling of pure CO_2 after absorption in NaOH solution, acidification and collection in a gas bag. Also ^{14}C specific activity values obtained using the cocktail with MPA had an average of 0.295±0.014 Bq/gC for bubbling of the combustion mixture directly from the bomb and of 0.296±0.010 Bq/gC respectively, for bubbling pure CO_2 from the gas bag. Due to the fact that the quality control material recommended by IAEA (IAEA-C3 Cellulose), used in our experiments, can be assimilated with the most of the vegetable materials, the preparation methods described can be considered as appropriate for radiocarbon environmental monitoring, especially due to the less time-consuming one involving direct bubbling from the combustion Parr bomb.

In the endowment of the Tritium Laboratory from ICSI Rm. Valcea, where the experiments where done, there is an oxygen combustion vessel produced by Parr Instruments USA, model 1121. The ability of the vessel 1121 to burn large quantities of the sample with full recovery of all combustion products (liquid and gaseous) makes it particularly effective for the determination of the elements present in small quantities in combustible materials or for the preparation of samples in order to determine the tritium and C-14 content. Slow burning samples can be burned into combustion vessel 1121 in quantities of up to 10 grams using

oxygen charging pressures up to 20 atm. These limits vary and must be checked experimentally for each sample. The sample size must be adjusted to an amount which will give complete combustion with peak pressures held in the range from 60 to 80 atm. The pressure should never exceed 100 atm. as an absolute maximum. Taking into account these limitations the ideal sample quantity was determined for the vegetable sample and basil essential oil. The complete combustion of the sample was determined using the $^{13}C/^{12}C$ isotope ratio measured in the initial sample and in the combustion gas mixture. In the first step, the minimum sample quantity required to obtain at least 3 grams of CO_2 needed to saturate the scintillation cocktail was calculated. The calculations were made taking into account the carbon content or the essential oil chemical formula. For the vegetable sample, a minimum amount of 20 g and 2 g for basil essential oil was calculated. Because the combustion vessel has limitations on the maximum sample amount, a series of experiments has been carried out to see if the minimum quantities required can be burned. Because the maximum pressures achieved for combustion of these quantities it was near the maximum allowable pressure another experiments were carried out to determine the ideal oxygen pressure in order to have complete combustion of the sample. For this, the oxygen charging pressure was gradually reduced and the $^{13}C/^{12}C$ isotopic ratio was measured in the initial sample and in the combustion gas mixture. From the analysis of the obtained data it can be observed that for both types of samples up to 17 atm. a complete combustion takes place. For the vegetable sample was reached a maximum pressure of 75 atm. 17 atm. charging pressure. This value is respect the Parr 1121 oxygen combustion vessel manufacturer's recommendations. For essential oil, the maximum pressure reached for 17 atm. charging pressure was 65 atm., a value that also respect the manufacturer's recommendations.

For documentation and management activities in the period between the project contracting and the Phase 1 deadline (October - December 2018), the following aspects were considered:

- Planning, monitoring, management and project coordination. Actions were taken to conclude the contract with the mentor and to acquire the equipment and materials needed to conduct the experiments from this stage of the project and to prepare the future ones;
- Literature study for the design of the experiments necessary to achieve the objectives of this stage.

Conclusion:

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