DEVELOPMENT OF DIRECT CO_2 ABSORPTION SYSTEM FOR RADIOCARBON DATING AND BIO-BASED CARBON DETERMINATION IN BIOGENIC-SYNTHETIC PRODUCTS

by

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Scientific paper
https://doi.org/10.2298/NTRP2204315S

This work presents a development of a new radiocarbon dating system based on CO_2 and liquid scintillation counting. The system is flexible enough to be applied in different fields such as radiocarbon dating (up to about 32 000 years span), environmental radioactive monitoring, and determining the fraction of biological carbon in environmentally-ecologically safe biodegradable and bio-synthetic products, and help accreditation to customaries.
The implemented system is developed following the standard method (ASTM D6866-06). It has been calibrated tested and verified for CO_2 production, absorption, and counting (using appropriate reference materials for the present-day, fossil, and in between ages). These results are optimistic that the developed system can contribute to the accreditation of ongoing and upcoming environment- friendly productions.

Key words: radiocarbon, CO_2 absorption, liquid scintillation counter, biobased carbon fraction, dating

INTRODUCTION

The ^{14}C is one of three naturally occurring carbon isotopes. It is radioactive with a half-life equal to 5730 years and decays by emitting a β-particle with an energy of about 156 keV. On the surface of the earth, the abundance of natural ^{14}C is very low (10^{-12}) relative to the other two stable carbon isotopes ^{12}C (98.9 %) and ^{13}C (1.1 %) [1]. The ^{14}C has two modes of production (natural and man-made). Natural production takes place due to nuclear reactions between cosmic rays neutrons and atmospheric nitrogen that gives a nearly constant rate of atom production, 2.5 $cm^{-2}s^{-1}$ [2]. The artificial man-made production takes place due to the thermonuclear tests that started in 1950 and generated high neutron flux which activated the atmospheric ^{14}N and produced ^{14}C. The production increased with the increase of the tests and reached its peak in 1963 as shown in fig. 1 [3]. The artificially produced ^{14}C activity has continually decreased on account of wash-out action by exchange with ocean sink. The combustion of fossil fuel (*e.g.* coal, petroleum) in the early 20th century led to a dilution of ^{14}C level due to the production of ^{14}C free carbon, Suess effect, this effect is also shown in fig. 1 [4, 5].

The produced radiocarbon either natural or man-made mixes with atmospheric carbon and is oxidized into CO_2 and passes through the natural carbon cycle, from the atmosphere to the biosphere, hydrosphere, and lithosphere, fig. 2 [6]. The atmospheric CO_2 is taken by plants through the photosynthesis process and reaches the soil zone through respiration or decay after a plant or animal death. The soil CO_2 can be dissolved with infiltrated water and reacts with soil carbonates to form inorganic carbon which reaches groundwater with organic carbon. Another part of the atmospheric CO_2 directly reaches the hydrosphere (rivers, lakes, sea, *etc*.) and exchanges with carbonaceous species and component, some are settled to the sea bottom, and also reaches the lithosphere through the transgression of seawater inland.

The balance between the production and decay of radiocarbon relatively amounts to the natural abundance of 10^{-12} which is equivalent to a value of 13.56 decay per minute per gram of carbon (dpm/g.c.) that represents the atmospheric carbon content of modern materials. This value is referenced to the time before 1890 (*i. e*., before industrial effects or nuclear effects). The percentage of the radiocarbon content to the value of 13.56 dpm/g.c. is called percentage modern carbon (pmc), which is the unit used for radiocarbon dating. The radiocarbon dates are determined by relating the radiocarbon content of the samples to that of the oxalic acid standard (OX1) which has 95 % of its activity equivalent to the 100 pmc, New oxalic acid standard (OX2) is being used which has 75 % of its activity equivalent to the 100 pmc [7]. The ^{14}C ages are re-

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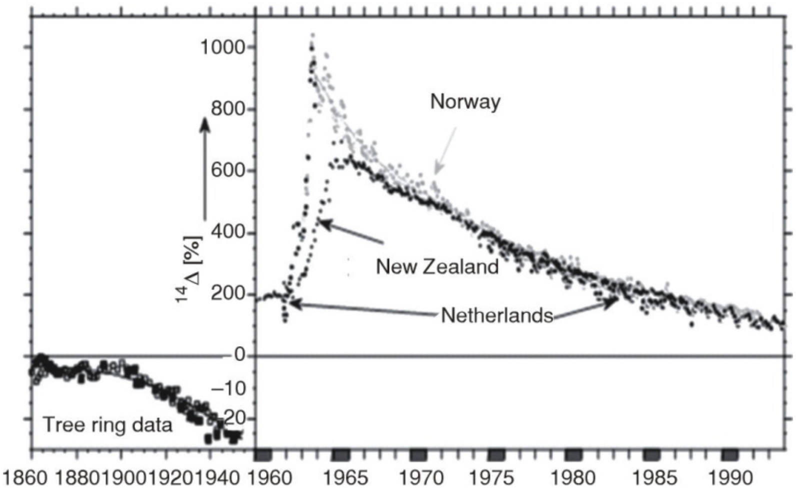

Figure 1. Radiocarbon content in atmospheric CO_2 [3]

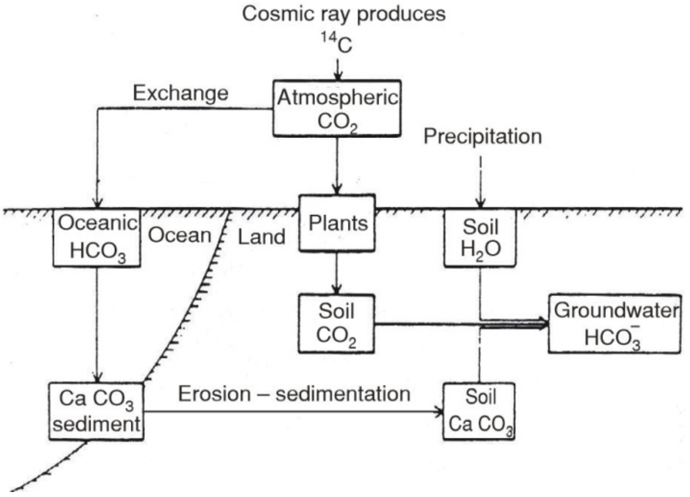

Figure 2. Natural cycle of carbon and ^{14}C [6]

ported as ^{14}C years BP, where the BP is before present (*i. e.* before 1950).

As much as living things are in contact with the atmosphere, they acquire the radiocarbon content which expresses the balance between production and decay. Once living things lose the contact with atmosphere either by death or burial deep underground (as groundwater when leaves the unsaturated zone), the loss due to radioactive decay will not be compensated. The radiocarbon content will exponentially decrease by decay according to its half-life time till it is completely lost after about 50 000 years (*i. e.* fossil fuels and geologically aged materials don't have radiocarbon in their content). Radiocarbon dating of carbonaceous material is based on measuring the exponential loss of atmospheric ^{14}C content, which starts at the time of atmospheric contact cut.

The recent increase in atmospheric CO_2 and the consequent effects on the global climate and environment have resulted in new interest in fossil carbon emissions and renewable sustainable resources (IPCC 2007) [8]. Within this framework, radiocarbon analysis is gaining ever-increasing importance as a well-established method for distinguishing the CO_2 gaseous emissions, the biogenic – recent content which is ^{14}C-rich from fossil component which is ^{14}C-absent. The growing promotion of and demand for renewable raw materials and environmentally friendly products (undoubtedly lead to the need for a standardized analytical protocol for traceability and labeling biobased products [9]. The CO_2 direct absorption method developed in this work can be applied to all carbon-based products and was approved by the american society for testing and material (ASTM) No. ASTM 6866 [10]. It is gaining increasing importance as a well-established method for distinguishing biogenic from fossil CO_2 and for certifying the biogenic fractions of biobased products.

EXPERIMENTAL WORK AND METHOD USED

The International Standard Test Methods for determining biobased content using ^{14}C analysis are three methods, that have been described in the ASTM D 6866 guidelines (ASTM International 2011, 2012). Method (A), Direct absorption of CO_2 and liquid scintillation counting is simple, safe, and results in significantly reduced analysis time and cost as compared to the other two methods.

The method can be used for organic and inorganic carbonaceous materials in air, water, soil, plants, sediments, oils, shells,…*etc*. It is reliable for radiocarbon dating in a range of maximum limits of 31 000 years, which corresponds to a combined uncertainty of 2 %, Curries 1995, (which is also defined by [9, 11-15] as < 2.2 % deviation from target value), standard deviation of 1.1 % and a relative error of 0.53. Recently, the method has been successfully used for the evaluation of ^{14}C activities in atmospheric and biological samples (Broni *et al*. 2009), for routine analysis of water samples in ^{14}C monitoring programs at nuclear power plants (Varlam *et al*. 2007), as well as for the certification of biobased products, which are presently of great concern (Noakes *et al*. 2006 and Norton and Devlin 2006). The indicated CO_2 absorption method has been developed in this work, according to the following steps:

The CO_2 is produced from the carbonaceous samples either by wet or dry combustion, it is then absorbed and chemically trapped as a carbamate in a suitable absorbing solution and gravimetrically measured, and analyzed by liquid scintillation counter (LSC) to determine the ^{14}C content. The developed apparatus is shown in fig. 3, it is composed of a gas production system (*e. g*. CO_2 derived from acid hydrolysis of carbonates or oxidative combustion bomb for organic samples) with an inlet for gas into decontamination and water removal traps, flow meter, vacuum pump, pressure gauge and absorbing solution (CarbosorbE® + Permaflour) in water ice bath [16].

The weighted CO_2 absorptive solution is radiocarbon measured using the low-background LSC, Quantulus 1220 by PerkinElmer. The liquid scintillation counter measures the energy released from the radioactive substance that activates the fluorochrome to the excited state. The fluorochrome then emits the energy as light photons that can be measured by photomultiplier tubes. The measurements take place as counts per minute that are calibrated into radioactivity using standards, spikes, and background. The preparation lines and the counting conditions established and followed in this work comply (with some modifications) with the optimized terms (^{14}C window, counting efficiency, figure of merits, quenching index) described in the article of Horvatinčić, *et al*. 2004 [17].

SYSTEM DEVELOPED AND RESULTS OBTAINED

The following four steps have been followed and the necessary flow lines have been developed for radiocarbon measurements using CO_2 absorption and liquid scintillation counting:

Carbon dioxide preparation from samples

The method used for CO_2 preparation from the sample for radiocarbon measurement depends on the nature of its carbon species (*i.e*. acid hydrolysis is used for inorganic carbon species and oxygen combustion is used for organic carbons). The samples used in this work are of organic carbonaceous origin, they are oxidized into CO_2 gas before analysis using an oxygen combustion bomb at a high pressure of about 30 atoms and electricity for ignition. The molecular weight of the carbon species of the samples determines the weight used for analyses. The weighted sample is put into the container in the high-pressure tank, then the electric circuit is closed between the electrodes of the tank lid and the samples inside it. The oxygen gas replaces the air in the tank and its pressure is regulated before combustion using an oxygen pump. One water sample from River Nile was used in this work as a representative of present-day radiocarbon concentration, its dissolved inorganic carbon (DIC) content was precipitated as $BaCO_3$ (using $BaCl_2$ in alkaline condition) which is dissolved using dilute phosphoric acid to get CO^2 liberated.

Figure 3. The system for CO_2 absorption

Carbon dioxide absorption

The system developed for CO_2 absorption is shown in fig. 3. It is matchable with the optimized work of Horvatinčić, *et al.* 2004 [17]. The storage steel container which contains the produced CO_2 gives the way to sequential decontamination traps (Silica Jell & KI/I2 & $AgNO_3$ & $K_2Cr_2O_7/H_2SO_4$) and dehydration trap (Liquid Nitrogen / Acetone) with a needle valve for regulating CO_2 flow rate. The system is interlinked with a vacuum pump, pressure gauges, absorbing solution, bubbler, and ice bath.

The whole absorption system is vacuumed before admitting the CO_2 gas into it. The CO_2 then passes through the decontamination and dehumidification traps. The CO_2 which is frozen into the liquid nitrogen trap is sublimed into a gas and passes under vacuum to the absorption/scintillation cocktail vial where is absorbed in the scintillation cocktail (10 ml:10 ml mixture of carbosorb and permafluor scintillator). The CO_2 flow rate is adjusted to a medium value of about 70 ml/min which is suitable for the gas to react and continue absorption till the absorption solution becomes saturated with CO_2 gas under equilibrium (in about 15 minutes + 10 minutes excess to assure saturation). The absorption process is exothermic, so the vial is put into an ice bath. The bubbles appear in the bubbler at the end of the line, indicating that the absorption mixture is almost saturated with CO_2. At the end of the process, the vial is removed from the line and weighed to gravimetrically determine the amount of the absorbed CO_2 and the degree of saturation of the amine.

The ^{14}C analysis using a liquid scintillation counter

The weighted CO_2 absorptive solution is radiocarbon measured using a LSC. The measurements take place in optimized conditions in terms of ^{14}C window, counting times, counting efficiency, and quenching index (SQP). The background of the instrument and the counting efficiency was determined using CO_2 derived from acid hydrolysis of limestone sample and combustion of oil samples. The present-day radiocarbon calibration was conducted by using CO_2 produced from acid hydrolysis of NIST Oxalic acid standard, Oxalic II (49960c). The optimized measuring conditions applied in this work are as follows: counting window was established to be between channels 140 and 375, the total counting time was set at 600 min to achieve statistical significance, and the BKG and STD count results in a counting efficiency of about 65 % which is comparable to reviewed optimized work.

System calibration and biogenic/fossil carbon determination

The amount of biobased carbon can be expressed as a fraction of sample mass or total carbon content. Products containing only carbon from fossil resources no longer have any ^{14}C activity and are reported as having a biobased content of 0 %. On the other hand, products containing only carbon from bio-renewable resources have a strong ^{14}C signature matching that of contemporary carbon sources and are reported as having a biobased content of 100 % [18]. Combining fossil carbon with modern carbon gives intermediate values for the biobased content, which are directly proportional to the concentration of modern carbon in the sample. The oxalic acid standard (OX2) has been used to qualify the modern radiocarbon while Oil and geologically aged limestone have been used to qualify the absence of radiocarbon in the fossil carbonaceous ones and present the background for the whole process. The (sugar and present-day Nile water) on one side and (polyethylene and petroleum oil) on the other side have been radiocarbon measured and used as end members for calibration.

A linear correlation Calibration Curve has been constructed, fig. 4, between the two end members of pure biogenic carbonaceous materials (represented by sugar and River Nile Water samples) and pure fossil synthetic carbonaceous material (represented by poly ethylene and petroleum oil samples). To validate the developed method, four samples have been prepared (as mixtures between sugar and polyethylene), these were used as test samples that showed a match of 0.988 with the end members calibration curve ($y = 0.0335x + 4.175$), fig. 5. Because of the good linear correlations reached in this work, it can be successfully used to quantitatively determine the biocarbon fraction in the present day produced biobased materials (using the count per minute (cpm) of the measured sample). Table 1 shows the average value of the triple samples' cpm, their uncertainty, and standard deviation, the values agree with previous work on the methodology.

CONCLUSIONS

A new method has been developed for sample treatment and liquid scintillation counting of radiocar-

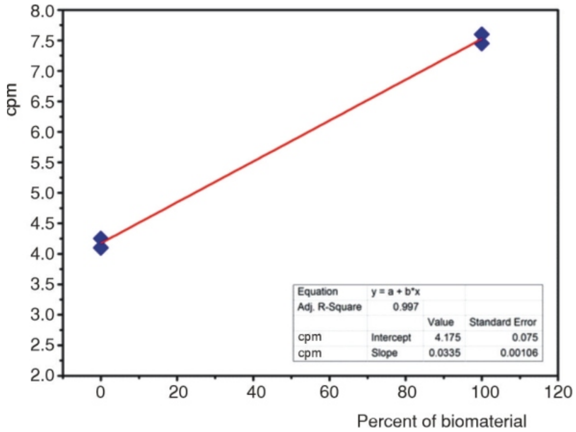

Figure 4. End members calibration curve of bigenic -synthetic radiocarbon

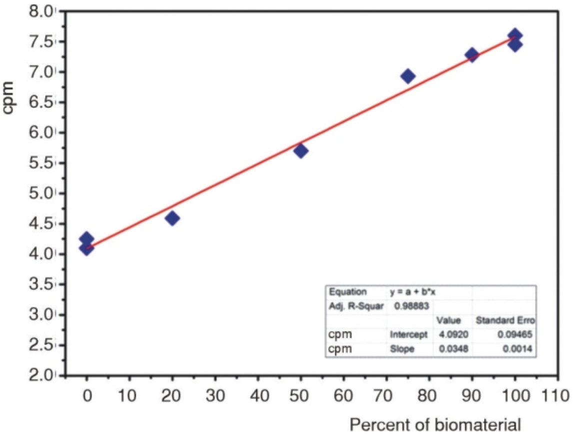

Figure 5. Verification curve for biobased carbon fraction

Table 1. Average cpm, uncertainty, and standard deviation of the study samples

Percentage of biogenic carbon	Average of cpm	Standard deviation	Uncertainty
0	3.983	0.104	0.060
20	4.373	0.025	0.015
50	5.650	0.050	0.029
75	6.857	0.051	0.030
90	7.283	0.075	0.043
100	7.523	0.075	0.043

bon content of carbonaceous samples. This is based on vacuum equilibrium absorption of samples CO_2 on carbamate – scintillator mixture. The developed method is simple, quick, and cheap and requires less carbon content in the measured samples (0.5 g).

The accuracy of the developed method is not high as that of the benzene synthesis method but is quite enough for important applications (*e. g.* geological and hydrogeological dating up to 32000 years, monitoring purposes at environmental levels, determination of bio-based fraction in bio-based materials, and other).

The developed system has been calibrated using standard carbonaceous materials that have ^{14}C content representing the two end members of the radiocarbon time scale (present- day origin and synthetic fossil origin). The system has been optimized and verified using check-test samples of mixing proportions in the range of the two end members, which show a 98 % match with the pattern of the two end members.

A CO_2 absorption system for radiocarbon measurements (using a liquid scintillation counter) has been developed in this work. It is ready for use for different types of environmental samples (air, water, plants, sediments, oils) in a wide range of applications. This work introduces a calibration curve ready for determining the biogenic carbon fraction of bio-based materials, directly using a strong linear relation, fitting a good coverage of standardized samples (mixtures between the two end members of the whole distribution).

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Received on August 19, 2022
Accepted on March 20, 2023

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РАЗВОЈ СИСТЕМА ДИРЕКТНЕ АПСОРПЦИЈЕ CO_2 ЗА РАДИОКАРБОНСКО ДАТИРАЊЕ И ОДРЕЂИВАЊЕ БИОЛОШКИ ЗАСНОВАНОГ УГЉЕНИКА У БИОГЕНО-СИНТЕТИЧКИМ ПРОИЗВОДИМА

Овај рад представља развој новог система радиокарбонског датирања заснованог на CO_2 и течном сцинтилационом бројању. Систем је довољно флексибилан да се може применити у различитим областима као што су радиокарбонско датирање (до око 32 000 година), праћење радиоактивности животне средине, одређивање удела биолошког угљеника у еколошки безбедним биоразградивим и биосинтетичким производима, а помаже и у акредитацији поступака.

Имплементирани систем развијен је по стандардној методи (ASTM D6866-06). Калибрисан је, тестиран и верификован за производњу CO_2, апсорпцију и бројање (користећи одговарајуће референтне материјале у садашње доба, фосилне и између доба). Ови резултати обећавају да развијени систем може допринети акредитацији текућих и будућих еколошки прихватљивих производа.

Кључне речи: радиоуг̄љеник, ап̄сорп̄ција CO_2, *т̄ечни сцинт̄илациони бројач, фракција биолошки заснованог̄ уг̄љеника, дат̄ирање*