

OPTIMIZATION OF ^{14}C CONCENTRATION MEASUREMENT IN AQUEOUS SAMPLES USING THE DIRECT ABSORPTION METHOD AND LSC

Carmen Varlam^{1,2} • Ioan Stefanescu¹ • Mihai Varlam¹ • Cristina Bucur³ • Irina Popescu¹ • Ionut Faurescu¹

ABSTRACT. We developed a radiocarbon measurement procedure for natural-level water samples. The characteristics and specifics of this new measurement technique are discussed and compared with concurrent methods. Several experiments were carried out for sample preparation; the direct absorption method was selected, with a few custom improvements, to increase the reproducibility and accuracy of this simple and quick method. Results confirmed the validity of the sample preparation and measurement procedures, and confirm that this method provides better reproducibility than traditional techniques. A validation test using CaCO_3 results from oyster shell and marble provided a mean value of 0.2137 ± 0.0039 Bq/g C, for an efficiency of ~64% and a background value of 2.22 cpm. This procedure was applied on different types of water.

INTRODUCTION

Radiocarbon is a radioactive isotope of carbon and is a pure beta emitter with a half-life of 5730 yr; it decays to ^{14}N by emitting low-energy beta radiation with an average energy of 49.5 keV and maximum energy of 156 keV. ^{14}C is easily transferred during biological processes and soil-plant interaction involving carbon compounds. Radioactive waste containing ^{14}C is continuously produced in nuclear reactors, spent-fuel reprocessing, and radioisotope production, as well as medical research.

Cernavoda Nuclear Power Plant (NPP) is the only NPP in Romania and the only Canada Deuterium Uranium[®] (CANDU) reactor operating in Europe. The Cernavoda Unit 1 is a pressurized heavy-water reactor (PHWR) fueled with natural uranium and moderated and cooled by heavy water. The radionuclide ^{14}C is a byproduct of this type of reactor and is predominantly produced by neutron activation of ^{17}O water molecules (heavy water is enriched not only in deuterium but also in ^{17}O). In heavy-water reactors such as the CANDU, the major portion of ^{14}C produced originates from the moderator. Routine operation of this type of reactor and its auxiliary process systems results in the production of a large variety of solid, liquid, and gaseous radioactive wastes.

Therefore, monitoring ^{14}C around this important nuclear facility has become a necessity, with water as the component of primary interest. In order to evaluate the release of ^{14}C from nuclear facilities, a background activity of 250 Bq/kg of stable carbon has been allowed by regulatory bodies such as the Institut de protection et de sûreté nucléaire (France), the National Radiological Protection Board (United Kingdom), and the Inspectorate for Nuclear Reactor Safety (Switzerland). According to these regulations, any ^{14}C level above this background level, other than normal production of ^{14}C by cosmic radiation, will be considered pollution (International Atomic Energy Agency 2004). Every monitoring program must include a background level of ^{14}C measurement on a routine basis to detect environmental increases from a particular source. Since the $^{14}\text{C}/^{12}\text{C}$ ratio in the present biosphere and atmosphere is only $\sim 10^{-12}$, substantial sample sizes are required to measure its activity with conventional β^- decay counting equipment. The CO_2 absorption method for preparing samples for ^{14}C analysis by liquid scintillation counting (LSC) has been successfully employed by several laboratories for many years. The method in our laboratory was developed by Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water and its main advantage is its

¹National Institute R&D for Cryogenic and Isotopic Technologies, Rm. Valcea, Romania.

²Corresponding author. Email: cvarlam@icsi.ro.

³Environmental Laboratory of NPP Cernavoda, Romania.

simplicity. As reported by Aravena et al. (1989), the method involves bubbling the CO₂ sample gas through a liquid cocktail containing the scintillator and the alkaline absorber, to the point of saturation. We report here on several routine procedures of this method in order to obtain reproducibility and accuracy. This method is applied to inorganic carbon from water samples.

METHODOLOGY

¹⁴C measurement using the direct absorption method follows similar principles to those of the benzene synthesis method. A known amount of carbon from sample standard or background material is counted as liquid in a liquid scintillation counter. The beta activity for the sample corresponding to its ¹⁴C decay is measured and compared to that of the background and modern standard. The only difference between the 2 methods is the way in which carbon from the sample, standard, or background is converted into liquid form before being measured in the scintillation counter. Both methods convert raw material to CO₂. Meanwhile, the benzene synthesis method converts the CO₂ to benzene with several intermediate steps (production of LiC and C₂H₂). In the direct absorption method, the CO₂ is bubbled through a liquid containing a tertiary amine, forming a liquid known as a carbamate that is usually mixed with a scintillation cocktail (C/S solution). For the direct absorption method, knowing the carbon amount is mandatory. Different laboratories are using various techniques of estimating the amount of carbon present in the sample. Some laboratories measure the amount of carbon in the C/S solution after bubbling, a practice that often may introduce larger errors in the overall determination of ¹⁴C. The method applied for these measurements ensures that the C/S solution was always saturated for samples, standards, and background. ¹⁴C analysis of water samples using the method of direct absorption of CO₂ in a mixture C/S solution has 4 stages.

The first stage is preparation, either as a scintillation cocktail mixture or as dissolved inorganic carbon (DIC) precipitated as barium carbonate. This step is carried out in 2 ways. Usually, Carbosorb E and Permafluor E⁺ (PerkinElmer, USA) can be used, but we do not obtain a saturated CO₂ solution using these materials, so it was necessary to prepare our own LS cocktail containing 2-Methoxyethylamine. To avoid any potential contamination from atmospheric CO₂ due to repeatedly opening the large container, the C/S was bottled in a single analysis vial, holding enough quantity for a single bubbling of a sample. For water samples analyzed for ¹⁴C, the DIC is precipitated as BaCO₃ slurry by adding BaCl₂ and NaOH. Thus, the DIC present in 20–100 L of water can be reduced in volume to less than 1 L.

In the second stage, barium carbonate from the water is acidified to release CO₂. The CO₂ is purified through a trap with AgNO₃ and cryogenic techniques to remove HCl vapor gases and tracer of water and is stored in a cylinder for 1–2 weeks (Figure 1). During this time, any radon in the CO₂ decays. The same procedure is applied for CaCO₃ from the standard (oyster shell) and background (marble).

The aim of the third stage is to absorb CO₂ in the form of carbamate in the C/S solution. To do this, the CO₂ is transferred to a bladder in the bubbling line (Figure 2). The transferred CO₂ is circulated for 10 min through the C/S solution in bubbler A. Cold water is necessary for trap A because conversion to carbamate is an exothermic reaction. Traps E and F with cold ethanol are used in order to recover any vapor of C/S solution. At first, CO₂ conversion to carbamate is rapid, but after several minutes it slows down as the saturation level is approached.

The last stage is measurement by LSC. A constant weight of C/S solution for each standard, background, and sample is obtained after a sufficient period of bubbling (i.e. steady-state or saturation level). This means that the same amount of carbon is present in each vial. The vials are then counted via conventional ¹⁴C analysis.

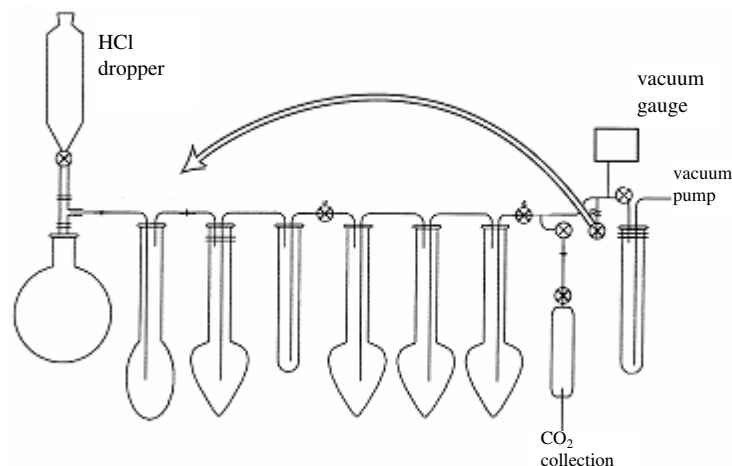


Figure 1 Schematic for CO_2 preparation line

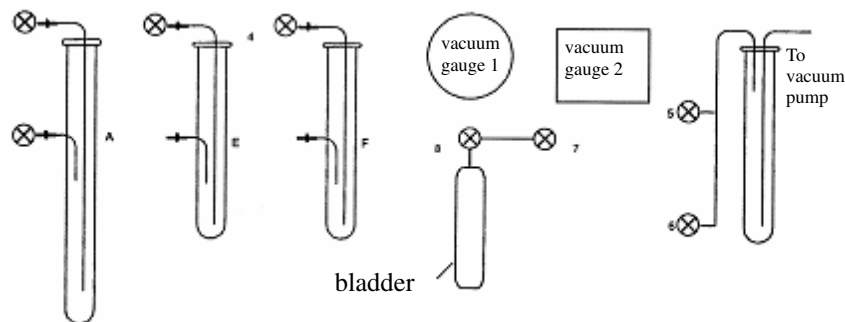


Figure 2 Schematic for bubbling line (no connecting tubing)

MEASUREMENT OF RADIOACTIVITY

The LS spectrometer used by our laboratory is a Quantulus 1220TM (Wallac Oy, Finland). Its features have been described in previous publications (e.g. Hemmila et al. 1994). The coincidence bias defines the minimum amplitude from which coincident pulses are accepted. For all measurements, we selected the highest coincidence bias. The pulse amplitude comparator (PAC), a device that discards pulses that differ in their amplitudes from left and right photomultipliers, has been set to 1. The optimal counting window corresponds to the highest figure of merit. We use a spectrum resolution of 1024 channels. The maximum corresponds to the window setting from channels 100–450.

The counting efficiency is not constant due to different reasons, including variation of intrinsic quenching, effect between vials, and variation in composition and volume of the counting solutions (Mestres et al. 1991). Due to the low-level conditions expected in the water samples (Varlam et al. 2001), we chose to use the internal standard method to establish counting efficiency. A known amount of nonquenching radioactive standard is added after a first sample count, homogenized well, then the sample is recounted. To estimate the validity of our procedure, we prepared a typical counting batch consisting of 1 procedural blank obtained from marble, 1 procedural standard obtained from oyster shell, 1 standard obtained from oyster shell, and a Wallac capsule with known ^{14}C activity. The ^{14}C standard capsule originated from an internal standard kit for LSC containing 103.000

dpm/capsule (Wallac, product No. 1210-122). The labeled compound (4- ^{14}C) cholesterol is produced by Amersham International (United Kingdom). The absolute activity of the capsules is calibrated by comparison with reference standards of (1- ^{14}C)-n-hexadecane supplied by NIST (SRM No. 4222C). For each typical batch, we checked the quench of prepared samples by using the spectral quench parameter of the external standard, SQP(E). The channel where the Compton electron spectrum ends is a qualitative indication that the measured samples have the same quench.

RESULTS AND DISCUSSIONS

The method described above relies on maintaining constant conditions to achieve reproducibility. To evaluate every stage of the routine procedure for ^{14}C measurement using the direct absorption method and LSC, we prepared several batches of oyster shell, marble, and capsule standard. Theoretically, ~ 1 g of carbon, in the form of DIC, is required in order to reach saturation with 20 g of C/S. We recorded initial pressure from the beginning of acidification (P_0), final pressure for obtaining CO_2 (P_f), mass of CO_2 obtained for each sample (m_{CO_2}), mass of C/S solution used ($m_{\text{C/S}}$), and mass of C/S after bubbling CO_2 .

Table 1 Parameters for preparing CO_2 from aqueous samples.

Sample type	P_0 (mbar)	P_f (mbar)	m_{CO_2} (g)	$m_{\text{C/S}}$ (g)	$m_{\text{C/S}}$ after bubbling (g)
Oyster 1	.030	21	14.87 ± 0.01	20.04 ± 0.01	23.72 ± 0.01
Marble 1	.031	21	12.59 ± 0.01	20.07 ± 0.01	23.76 ± 0.01
Standard 1	.030	22	14.79 ± 0.01	20.02 ± 0.01	23.69 ± 0.01
Oyster 2	.031	20	14.91 ± 0.01	20.05 ± 0.01	23.78 ± 0.01
Marble 2	.032	20	12.51 ± 0.01	20.04 ± 0.01	23.64 ± 0.01
Standard 2	.031	21	14.81 ± 0.01	20.02 ± 0.01	23.67 ± 0.01
Oyster 3	.031	21	14.92 ± 0.01	20.05 ± 0.01	23.65 ± 0.01
Marble 3	.030	21	12.47 ± 0.01	20.04 ± 0.01	23.70 ± 0.01
Standard 3	.030	22	14.84 ± 0.01	20.07 ± 0.01	23.71 ± 0.01
Oyster 4	.032	21	14.77 ± 0.01	20.02 ± 0.01	23.64 ± 0.01
Marble 4	.031	22	12.55 ± 0.01	20.04 ± 0.01	23.68 ± 0.01
Standard 4	.032	21	14.96 ± 0.01	20.08 ± 0.01	23.72 ± 0.01
Oyster 5	.031	21	14.85 ± 0.01	20.07 ± 0.01	23.75 ± 0.01
Marble 5	.031	20	12.63 ± 0.01	20.06 ± 0.01	23.71 ± 0.01
Standard 5	.031	21	14.72 ± 0.01	20.06 ± 0.01	23.66 ± 0.01

Applying routine procedures for obtaining samples to be measured in a LS counter (Table 1), we prepared a mean mass of CO_2 : $\sim 14.84 \pm 0.01$ g for oyster shell and $\sim 12.54 \pm 0.01$ g for marble. Special care was given to the purification line in order to avoid any isotope fractionation during sample acidification and cryogenic transfer. Each CO_2 sample obtained was measured by mass spectrometry and the following values were determined: oyster shell $\delta^{13}\text{C} = 0.82\text{‰}$; marble $\delta^{13}\text{C} = 2.42\text{‰}$. A mean of 3.64 g of CO_2 was fixed in the C/S solution.

Samples, standard, and background were transferred in 20-mL low-background glass vials with Teflon[®]-coated caps and counted in the Quantulus for 1000 min (100 min/cycle). The counting efficiency at the best factor of merit ($A_{\text{std}}/B^{1/2}$) is $\sim 64\%$, where A_{std} is the normalized net count rate of the standard and B is the background count rate. Using this configuration, we measured 5 batches of standard, background, and oyster shell (Table 2). Our absolute counts of the marble sample provided

an average value of ± 2.225 counts per minute (cpm) ($n = 10$), which translates to 0.005 Bq using a 64% conversion for the efficiency.

Table 2 Oyster shell specific activity of ^{14}C .

Sample type	Mean count rate (cpm)	Efficiency (%)	Figure of merit	SQP(E) (channel)	Specific activity (Bq/g C)
Oyster 1	10.750 ± 0.104	64.12	1851	704.82	0.2217 ± 0.0022
Marble 1	2.222 ± 0.047	64.12	1851	702.68	—
Standard 1	$66,045.195 \pm 46.920$	64.12	1851	707.11	—
Oyster 2	10.095 ± 0.100	64.98	1877	702.21	0.2129 ± 0.0021
Marble 2	2.249 ± 0.047	64.98	1877	701.73	—
Standard 2	$66,929.422 \pm 47.233$	64.98	1877	709.40	—
Oyster 3	10.572 ± 0.103	63.18	1831	712.01	0.2187 ± 0.0021
Marble 3	2.314 ± 0.048	63.18	1831	701.66	—
Standard 3	$65,927.889 \pm 46.878$	63.18	1831	701.93	—
Oyster 4	10.641 ± 0.103	64.69	1849	700.07	0.2167 ± 0.0021
Marble 4	2.104 ± 0.048	64.69	1849	701.06	—
Standard 4	$66,456.342 \pm 47.066$	64.69	1849	704.56	—
Oyster 5	10.328 ± 0.102	63.74	1823	699.71	0.2192 ± 0.0021
Marble 5	2.237 ± 0.047	63.74	1823	709.03	—
Standard 5	$66,341.784 \pm 47.025$	63.74	1823	710.86	—

Applying the Student's t test of significance, the measured values of oyster shell ^{14}C activity are around the mean of 0.2178 ± 0.0039 Bq/g C. The SQP(E) parameter indicates the same quench of prepared samples, its variation within 1% of the accepted counting error. The oyster shell value using this procedure is in accordance with the known ^{14}C activity in the environment.

Using the routine procedure, we measured different types of water: surface, drinking, underground, and seawater (Table 3). Measuring seawater was necessary because the NPP is located 64.4 km from the Black Sea.

Table 3 Specific activity of ^{14}C for different types of water.

Sample type	Mean count rate (cpm)	Efficiency (%)	Figure of merit	SQP(E) (channel)	Specific activity (Bq/g C)
Surface water 1	9.696 ± 0.098	63.18	1831	697.35	0.1966 ± 0.0033
Surface water 2	9.749 ± 0.099	63.18	1831	703.22	0.1979 ± 0.0033
Drinking water 1	9.018 ± 0.095	63.74	1823	696.89	0.1696 ± 0.0032
Drinking water 2	9.271 ± 0.096	63.74	1823	704.61	0.1734 ± 0.0032
Underground water 1	7.052 ± 0.084	64.69	1849	693.24	0.1361 ± 0.0031
Underground water 2	7.063 ± 0.084	64.69	1849	701.13	0.1363 ± 0.0031
Seawater 1	11.103 ± 0.105	64.12	1851	706.56	0.2374 ± 0.0034
Seawater 2	11.172 ± 0.106	64.12	1851	699.18	0.2398 ± 0.0034

In order to have at least 2 g of carbon for ^{14}C analysis, we sampled ~60 L of water/sample. One problem was that the seawater had a SO_4^{-2} concentration of 1349.7 mg/L. This procedure can be applied to different types of water and yields good sensitivity and reproducibility.

CONCLUSION

The CO₂ absorption technique presented yields reproducible results with a constant level of quenching represented by an independently determined spectral quench parameter, SQP(E), using an external standard. The procedure designed for routine analysis was validated using CaCO₃ from oyster shell and marble. A mean value of 0.2137 ± 0.0039 Bq/g C was obtained, for an efficiency value of ~64% and a background around 2.22 cpm. This procedure can be applied in monitoring programs because it is less time consuming than benzene synthesis.

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