APPLYING THE DIRECT ABSORPTION METHOD AND LSC FOR ^{14}C CONCENTRATION MEASUREMENT IN AQUEOUS SAMPLES

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ABSTRACT. We investigated a simple, reliable radiocarbon measurement procedure for water samples using the direct absorption method for sample preparation, followed by low-level liquid scintillation spectrometry. This process has involved quantitative evaluation of the conversion steps in order to estimate the appropriate working parameters. The ^{14}C activity of dissolved inorganic carbon (DIC) for several types of water (ranging from seawater to groundwater) has been measured, paying attention to the preparation requirements of each type of water. The main advantage of this method is the simplified sample preparation, allowing measurement of a great number of samples in less time. This method was designed for routine analysis of water samples, and it is proposed particularly for use in ^{14}C monitoring programs of CANDU-type reactors.

INTRODUCTION

Prior to recent man-induced changes to the carbon cycle, the amount of carbon in the different reservoirs on earth (such as the atmosphere, ocean, and biosphere) was stable or slowly drifting during glacial to interglacial transitions. Today, the impact of human activities and the size of the reservoirs are changing quickly. Fossil fuels are burned on a large scale, forest areas are converted to grasslands and vice versa, deserts are increasing in size, and nutrients on land and in coastal seas are more widely available as a result of fertilizer production. When these effects are combined with anthropogenic radiocarbon, wide-ranging monitoring programs such as that for the area surrounding the Cernavoda nuclear plant are required in order to evaluate potential negative impacts on the ecosystem.

Cernavoda nuclear power plant (located about 64 km from the Black Sea coast) is the only nuclear power plant in Romania and the only CANDU™ (Canada deuterium uranium) reactor operating in Europe. It uses heavy water (deuterium oxide) as a moderator and coolant and natural uranium for spent fuel. Cernavoda NPP consists of Unit 1 (714 Mw), and by the end of 2006 a second unit (707 Mw) will be operational. A third and fourth similar units are planned to be developed by 2010. The potential environmental disturbance generated by nuclear power plants in general is already a well-known issue and will become an increasingly important concern for the human community. Therefore, the geographic areas around these installations are categorized by natural features where there are significant risks to the water and soil, and by atmospheric degradations from nuclear activities, of particular interest for heavy-water nuclear reactors. The radionuclide ^{14}C is a byproduct that results predominantly by neutron activation of [17]O water molecules (because heavy water is enriched not only in deuterium but also in heavy isotopes of oxygen). In heavy-water reactors such as CANDU, the major portion of ^{14}C produced originates from the moderator. Most of the available techniques for ^{14}C removal from gaseous streams remove ^{14}C as CO_2. The main disadvantage of these methods is that a large amount of secondary waste is generated if the waste stream contains considerable amounts of [12]CO_2. Although methods for the separation of [14]CO_2 and [12]CO_2 are available, they are relatively costly. No specific study has been carried out for the removal of ^{14}C from liquid streams, although most of the conventional liquid treatment methods can remove ^{14}C as bicarbonate and carbonate. Since more stringent environmental regulation can be expected in the future due to the installation of new operating units, specific studies of ^{14}C from liquid waste and its impact on the environment are strongly required.

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Romanian governmental regulations on releases of radioactive substances into the environment are usually based on radiation protection concerns. Severe restrictions apply to the discharge of alpha and beta emitters. [14]C discharge at considerably elevated levels from Cernavoda NPP have been studied by direct measurements of ^{14}C levels both in the effluents themselves and in the environment (Cernavoda Nuclear Power Plant 2003; Bobric et al. 2003). These studies, however, have concentrated largely on determining ^{14}C release rates from this specific nuclear installation and atmospheric dispersion models. Recently, monitoring ^{14}C around this important nuclear facility became a necessity, with water resources being 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. According to these regulations, any ^{14}C level above this background level, other than the normal production of ^{14}C by cosmic radiation, will be considered pollution (International Atomic Energy Agency 2004). Thus, every monitoring program must determine a background level of ^{14}C measurement on a routine basis to detect environmental increases from a particular source.

Since the ^{14}C/^{12}C ratio in the present biosphere and atmosphere is on the order of only 10^{-12}, substantial sample sizes are required to measure its activity with conventional β^- decay counting equipment used in the nuclear research industry. Over the last decade, the CO_2 direct absorption method for preparing samples for ^{14}C analysis by liquid scintillation counting (LSC) has been successfully employed in many laboratories, primarily for dating groundwater. The method employed in our laboratory is a follow-up of the measurement procedure developed by CSIRO Land and Water. The main advantage of the direct absorption method is its simplicity. Vita-Finzi and Leaney (2006) provide a summary of the development of the direct absorption method for ^{14}C dating. In their study, they also give modifications to the "continuous circulation" approach to the direct absorption method originally presented (Leaney et al. 1994). This paper reports on the installation commissioning and testing of the method in our institute. Furthermore, we discuss several routine procedures of this method in order to obtain reproducibility and accuracy. The method described in the following has been currently applied to inorganic carbon from different types of water samples: drinking, surface, underground, and seawater.

METHODS, EQUIPMENT, AND MATERIALS

[14]C measurement using the direct absorption method follows similar principles to those used in the benzene synthesis method. A known amount of carbon from a sample standard or background material is counted as liquid in a liquid scintillation (LS) counter. The beta activity for the sample corresponding to its ^{14}C 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 CO_2. The next phase following CO_2 production in the benzene synthesis method is the CO_2 conversion to benzene with several intermediate steps (production of LiC and C_2H_2). In the direct absorption method, the CO_2 is bubbled through a liquid containing a tertiary amine (2-methoxyethylamine) mixed with a scintillation cocktail, thus forming a liquid known as a carbamate. Therefore, for this method, the knowledge of the carbon amount is mandatory. Various techniques have been used in different versions of the direct absorption method to estimate the amount of carbon from the sample present in the carbamate. Some of them measure the amount of carbon in the carbamate after bubbling, a practice that often is subject to large errors in the overall determination of [14]C. The method routinely applied in our laboratory for these measurements was to ensure that the carbamate solution is always saturated for samples, standards, and background. [14]C analysis of water samples using this method has basically 4 stages, described in the following.

The first step is to prepare a homogenous mixture of 2-methoxyethylamine and scintillant. The second step involves precipitation of the DIC from the water sample as $BaCO_3$ slurry by adding $BaCl_2$ and NaOH. In this way, the DIC present in 20–100 L of water is reduced to a volume less than 1 L. For the described method, a minimum of 2.6 g of CO_2 is required as DIC in the water sample. For this reason, the required amount of water was determined by considering the concentration of HCO_3^- and dissolved CO_2 in the water sample. This can be approximated as shown in Figure 1.
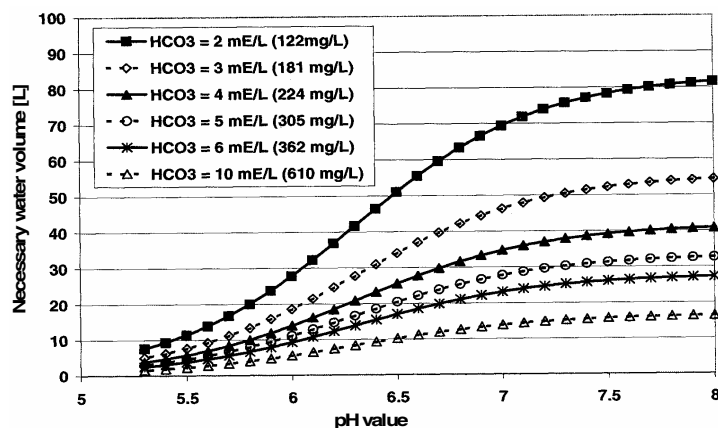

Figure 1 Necessary amount of water as a function of pH and HCO_3^- content

In the third stage of the method, barium carbonate from water is acidified to release CO_2. The CO_2 is purified via a trap with $AgNO_3$ and the cryogenic technique is used to remove HCl vapors and traces of water. A similar procedure is applied to generate CO_2 from $CaCO_3$ using standard carbonate material (modern marine shell) and background carbonate material (marble) (Figure 2). The CO_2 is then stored in a cylinder for 1–2 weeks during which time any radon in the resulting CO_2 will decay. An alternative procedure to remove radon has recently been described by Vita-Finzi and Leaney (2006). In their revised method, radon is removed by bubbling nitrogen gas through the carbamate solution, thus eliminating the time required for radon to be removed by radioactive decay. In our laboratory, we have not adopted this revised methodology.

The goal of the fourth stage is to absorb CO_2 in the form of carbamate and to ensure that exactly the same amount is absorbed for each sample, standard, and background (Figure 3). The routine approach to achieve this task is to transfer CO_2 to a bladder in the bubbling line and to circulate it for 10 min through the carbamate solution. During this time, the amount of CO_2 present in the bladder decreases as it is absorbed. Utilization of a bladder ensures that complete saturation takes place and also ensures that the carbamate solution is maintained at atmospheric pressure. A water cooling system has been used for this operation as conversion to carbamate is an exothermic reaction. At the beginning, CO_2 conversion to carbamate is fast, but within a several minutes it slows down as saturation is approached.

The last stage is measurement by LSC. A constant weight of carbamate solution for each standard, background, and sample is used. This ensures that the same amount of carbon is present in each vial. The vials are then counted via conventional ^{14}C analysis.

The LS spectrometer used by our laboratory is the Quantulus 1220™ from LKB-Wallac Oy. Its features have been described in previous publications (e.g. Hemmilä et al. 1994). The coincidence bias

Figure 2 Line for BaCO$_3$ acidification and CO$_2$ purification

Figure 3 Bubbling line for CO$_2$ absorption

that defines the minimum amplitude from which coincident pulses are accepted has been set at the "high" level. The pulse amplitude comparator (PAC), a device that discards the pulses that differ in amplitude from the left and right photomultipliers, has been set to 1. The optimal counting window corresponds to the highest figure of merit (FM), which for our counter is a channel window of 100 to 400.

Leaney et al. (1994) suggest that, providing clean and dry CO$_2$ is produced and the bubbling system is maintained at atmospheric pressure, there is no need to correct for quenching or the amount of CO$_2$ absorbed during LSC. However, for our system we noted that the counting efficiency was not constant due to several identified factors, such as variation of intrinsic quenching, the effect between vials, variation in composition, and volume of the counting solutions (Mestres et al. 1991). Due to

the low-level radioactivity expected in the water samples (Varlam et al. 2001), we decided on using the internal standard method to establish counting efficiency. A known amount of nonquenching radioactive standard was added after initial sample counting. The solution was then shaken so as to be well homogenized, and then recounted. A typical method validation counting batch was prepared consisting of 1 procedural blank obtained from marble, 1 procedural standard obtained from marine shell, 1 standard obtained from marble, and a Wallac capsule with known ^{14}C activity. This ^{14}C standard capsule originates 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 batch, we check the quench of prepared samples by using the spectral quench parameter of the external standard, SQP(E). The channel number where the Compton electron spectrum ends is considered as the qualitative indication for the identical quench of every measured sample.

RESULTS

The method described above relies on maintaining constant conditions to achieve good reproducibility. In order to evaluate every stage described above for ^{14}C measurement using the direct absorption method and LSC, several batches of oyster shell, marble, and capsule standard have been prepared. Applying the validation procedure (Varlam et al. 2006), we establish a mean activity for marine shell of 0.2178 ± 0.0039 Bq/g C, or 114.18 ± 1.82 pMC.

Theoretically, an estimated 1 g of carbon (in the form of DIC) is required to reach saturation with 20 g of scintillation liquid. To avoid any problem during sample preparation, a large enough amount of water has been sampled to allow the precipitation of 2 g of carbon as $BaCO_3$. HCO_3^- specie is dominant (Table 1), varying from 78 mg/L (drinking water 2) to 234 mg/L (surface water 1).

Table 1 Physical and chemical characterization of aqueous samples.

Sample type	pH	Conductivity (mSv/cm)	Anion and cation concentrations (mg/L)							
			Cl	Ca	Mg	Na	K	HCO_3	CO_3	SO_4
Seawater 1	8.07	20.6	817.9	368	415.6	292.6	189	167	18	1580
Seawater 2	8.09	23.2	724.8	325.1	182.5	362.1	245.6	178	35.1	1860
Drinking water 1	7.30	0.732	80.3	72.8	38.90	45.90	6.8	116	12.2	46
Drinking water 2	7.94	0.938	106.35	64.1	44.6	72.5	27.9	78	7.2	98.6
Underground water 1	7.89	2.98	336.8	75.0	36	148.2	77.9	463.6	48	230.2
Underground water 2	7.5	1.728	478.6	42.5	257	83.72	13	189.1	6	30
Surface water 1	7.26	0.751	36.99	55.7	10.20	23.40	6.8	234	6.1	42
Surface water 2	7.69	0.746	60.4	38.6	91.2	11.2	274.5	198	38.6	189

The sulfate content in water influenced the resulting barium carbonate precipitate. Barium chloride also reacts with the sulfate from water and forms barium sulfate, influencing the total precipitation of carbonates and bicarbonates. For this reason, for waters that contained large amounts of sulfates (like seawater), it was necessary to use larger quantities of barium chloride than those previously mentioned (see Table 2).

Table 2 Necessary quantity and quantity used of $BaCl_2\ 2H_2O$ for each type of sample.

Sample type	Necessary quantity (mg/L)	Quantity used for each type of water sample (mg/L)
Seawater 1	4744.58	Function of sulfate concentration
Seawater 2	5567.54	
Drinking water 1	630.28	4500 mg/L
Drinking water 2	591.18	
Underground water 1	2633.31	4500 mg/L
Underground water 2	857.01	
Surface water 1	1067.47	4500 mg/L
Surface water 2	1428.02	

Applying this routine procedure for sample conversion to CO_2 and measuring it using the LS method, the mean mass of CO_2 was obtained for the following: ~5.44 g for seawater, ~3.87 g for drinking water, ~6.18 g for underground water, and ~5.71 g for surface water. We also recorded the CO_2 mass obtained for each type of sample, the differences in mass for each sample, the mass of the scintillation liquid used, and the mass of carbamate solution after bubbling. From the difference of the mass of carbamate solution after bubbling and the mass of carbamate solution used, a mean value was calculated of 3.70 g for CO_2 fixed in the carbamate solution.

In order to have at least 2 g of carbon for ^{14}C analysis, about 60 L of water/sample has been sampled. Of particular concern is the Black Sea water. The Black Sea is the biggest anoxic marine system in the world. It does not contain oxygen deeper than 200 m and includes sulfuric hydride. A concentration of SO_4^{-2} of 1580 mg/L is usually found in this seawater. Special attention was necessary for the production of CO_2 due to the large precipitate quantities used in this stage.

Samples, standard, and background were transferred in 20-mL low-background glass vials with Teflon® inserts placed inside the caps and were counted in a Quantulus LS counter for 1700 min (17×100 min/cycle). The counting efficiency at the best factor of merit ($A_{std}/B^{1/2}$) was ~64.98%, where A_{std} is the normalized net count rate of the standard and B is the background count rate (Figure 4). Our absolute counts of marble sample provided an average value of 2.249 ± 0.047 cpm, which translates to ~0.005 Bq using a 64.98% conversion for the efficiency.

Using the described configuration, we measured batches of standard, background, and water samples. A typical ^{14}C measurement spectrum for underground water using the LS method is given in Figure 5.

Measured values for different types of water (Table 3) vary between 0.1436 ± 0.0020 Bq/g C for underground water to 0.2288 ± 0.0034 Bq/g C for seawater—similar to the values usually found in the environment. The SQP(E) parameter indicates the same quench of prepared samples without differences between types of sample, its variation being within 1% of the accepted counting error interval. Variation between different samples of the same water type was within the estimated and measured uncertainty interval.

It is not the intention of this paper to extensively discuss the results obtained; however, a few considerations could be made related to the ^{14}C level of the sampling points. All samples are from June 2005. Surface water was sampled from Danube Black Sea canal before the NPP Cernavoda was built, and drinking water samples were tap water from the Cernavoda location. The reported values are practically in the same range because both water sample types have the same origin, the Danube
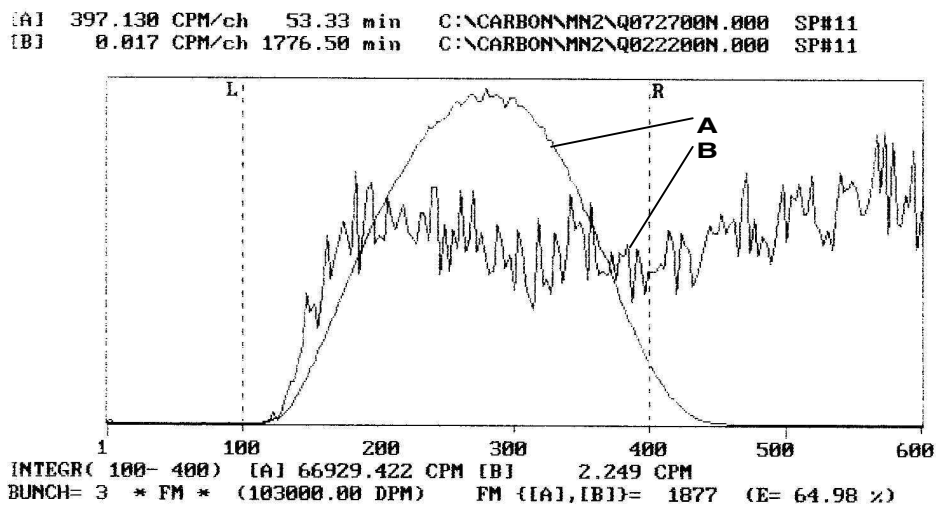
```
[A]   397.130 CPM/ch    53.33 min   C:\CARBON\MN2\Q072700N.000   SP#11
[B]     0.017 CPM/ch  1776.50 min   C:\CARBON\MN2\Q022200N.000   SP#11
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INTEGR( 100- 400)  [A] 66929.422 CPM [B]     2.249 CPM
BUNCH= 3  * FM *  (103000.00 DPM)   FM {[A],[B]}=  1877  (E= 64.98 %)
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Figure 4 Counting efficiency for [14]C samples using Quantulus LSC: A) internal standard spectrum for known activity of [14]C; B) marble spectrum.

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[A]   397.130 CPM/ch    53.33 min   C:\CARBON\MN2\Q072700N.000   SP#11
[B]     0.017 CPM/ch  1776.50 min   C:\CARBON\MN2\Q022200N.000   SP#11
[C]     0.063 CPM/ch  1688.32 min   C:\CARBON\MIN0\Q042400N.000   SP#11
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INTEGR( 100- 400)  [A] 66929.422 CPM [B]     2.249 CPM [C]    7.849 CPM
BUNCH= 3  * Bq *  (103000 DPM)   Net Activity of [C] = 0.1436± 0.0020 Bq
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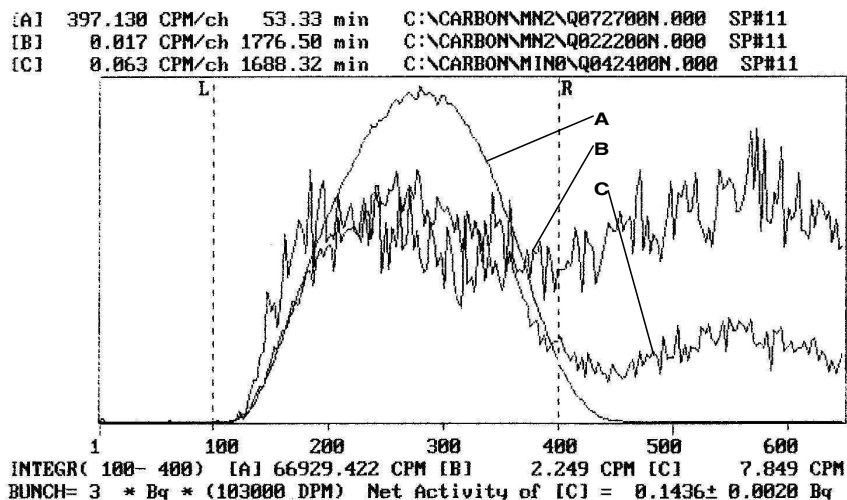
Figure 5 [14]C spectrum for underground water: A) internal standard spectrum for known activity of [14]C; B) marble spectrum; C) unknown sample spectrum of [14]C.

River. Underground water was sampled from the Seimeni well. Seimeni is a village near the evacuation canal of NPP Cernavoda, on the east side of the Danube. The recorded values of 77–78 pMC are typical values for shallow water. There are no reported values for [14]C levels in the area aquifer before the nuclear power plant commissioning in December 1996. The reported values for [14]C in atmospheric CO_2 (Davidescu et al. 2002) for Cernavoda indicate an increasing trend during 1996–2001. The range was between 116.3 ± 0.8 and 132.0 ± 2.0 pMC in 2001. Seawater was sampled from Cherhana Agigea (where the Danube Black Sea canal flows into the Black Sea). Before the introduction of bomb [14]C, the DIC in ocean surface layer had a [14]C activity of ~95 pMC. The very sudden increase in atmospheric [14]C activity and its uptake by the ocean raised the [14]C activity to ~110 pMC in the surface layer (Druffel et al. 1992). The recorded value of 123.97 ± 2.22 pMC can be explained

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

Sample type	Mean count rate (cpm)	Efficiency (%)	FM	SQP(E) (channel)	Specific activity (Bq/g C)	pMC
Standard	66,929.422 ± 35.42	64.98	1877	702.17	—	—
Marble	2.249 ± 0.035	64.98	1877	700.68	—	—
Surface water 1	9.796 ± 0.075	64.98	1877	697.35	0.1935 ± 0.0033	105.10 ± 1.98
Surface water 2	9.749 ± 0.075	64.98	1877	703.22	0.1932 ± 0.0033	104.44 ± 1.97
Drinking water 1	9.191 ± 0.073	64.98	1877	696.89	0.1781 ± 0.0032	96.58 ± 1.87
Drinking water 2	9.143 ± 0.073	64.98	1877	704.61	0.1734 ± 0.0032	95.92 ± 1.86
Underground water 1	7.872 ± 0.068	64.98	1877	693.24	0.1461 ± 0.0020	78.33 ± 1.64
Underground water 2	7.840 ± 0.068	64.98	1877	701.13	0.1436 ± 0.0020	77.88 ± 1.63
Seawater 1	11.103 ± 0.081	64.98	1877	706.56	0.2271 ± 0.0034	123.01 ± 2.21
Seawater 2	11.172 ± 0.081	64.98	1877	699.18	0.2288 ± 0.0034	123.97 ± 2.22

by waste-water evacuation of NPP Cernavoda. The described method has been proven to be suitable for extensive ^{14}C monitoring studies involving a large number of water samples.

CONCLUSION

The presented CO_2 absorption technique 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 applied for different types of water, with measured values being between 0.1436 ± 0.0020 Bq/g C (77.88 ± 1.64 pMC) for underground water and 0.2288 Bq/g C (123.97 ± 2.22 pMC) for seawater. Evaluating the specific activity of ^{14}C in water samples is important for environmental impact assessment. This procedure can be applied in monitoring programs since it is less time consuming and less expensive than benzene synthesis.

The estimated increase of the ^{14}C level in the environment can be confirmed only by an extensive monitoring program in which water is one of the most important samples. Using the ^{14}C signal for the Cernavoda area, it can also be applied in hydrological studies, but with an additional stage for standard validation (in our case, marine shell). Due to the different batches of scintillation cocktail that will be prepared in laboratory, it is necessary to have a carbamate prepared from standard carbonate and background carbonate material in each ^{14}C run and to use an SQP(E) as a qualitative indicator of the sample preparation procedure.

ACKNOWLEDGMENTS

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