UPGRADE OF THE CO_2 DIRECT ABSORPTION METHOD FOR LOW-LEVEL ^{14}C LIQUID SCINTILLATION COUNTING

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ABSTRACT. A new system for CO_2 absorption and liquid scintillation counting (LSC) was designed and developed along with its inherent measurement protocol for radiocarbon analysis in gaseous emissions, fuels, and biobased products. CO_2 is chemically trapped as a carbamate in a suitable absorbing solution (3-methoxy-propyl-amine), gravimetrically measured, and analyzed by LSC (using a Quantulus™ 1220) to determine the ^{14}C content. The use of cryogenic traps and a pressure transducer in the system prevents the need for closed-loop recirculation or additional steps to maximize CO_2 capture in a short amount of time. The choice of PTFE vials used both for CO_2 pretreatment and subsequent LSC analysis provides the opportunity to significantly reduce the background counting down to 40% with respect to the low-^{40}K glass vials. This upgrade resulted in improving the maximum detectable age back to 36,000 yr BP in routine measurements. This method therefore turns out to be flexible enough to be applied for ^{14}C dating as well as to differentiate between modern and fossil carbon.

INTRODUCTION

The recent increase in atmospheric carbon dioxide (CO_2) and the consequent effects on the global climate and environment have resulted in new interest in fossil carbon emissions and renewable and sustainable resources (IPCC 2007). Within this framework, radiocarbon analysis is gaining ever-increasing importance as a well-established method for distinguishing biogenic (^{14}C-rich) from fossil (^{14}C-poor) CO_2 in gaseous emissions. This approach is also useful in the field of renewable energy resources where biobased carbon fuels are very attractive because they can be associated with a virtually neutral carbon balance. From this perspective, ^{14}C analysis could be helpful, when suitable, for budgeting CO_2 emissions with the goal of preventing or limiting taxation under a carbon-emissions trading system (IPCC 2005).

The USA BioPreferred® Program (http://www.biopreferred.gov/) and the European Ad-hoc Advisory Group for Bio-based Products (http://ec.europa.eu/enterprise/policies/innovation/policy/lead-market-initiative/biobased products/index_en.htm) aim to promote the purchase and use of certified biobased products. The growing promotion of and demand for renewable raw materials and environmentally friendly products (Noakes et al. 2006; Norton and Devlin 2006; Onishi et al. 2010) undoubtedly lead to the need for a standardized analytical protocol for traceability and labeling of biobased products.

The International Standard Test Methods for determining biobased content using ^{14}C analysis have been described in the ASTM D6866 guidelines (ASTM International 2011, 2012). We describe in detail here the 3 official analytical protocols for ^{14}C determination. These test methods are applicable to any product containing a carbon-based component that can be turned into CO_2 gas by combustion. The 3 test methods are 1) accelerator mass spectrometry (AMS); 2) benzene-LSC (liquid scintillation counting); and 3) CO_2 cocktail-LSC.

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All 3 approaches require the production of CO_2 by a combustion step 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-LSC 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-LSC 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. The principal absorbent typically used for this application is Carbo-Sorb® E (Perkin-Elmer), which is able to chemically trap 4.8 mM of CO_2 for 1 mL of solvent as a carbamate. LSC counting is subsequently carried out after mixing with a proper scintillator (Permafluor® E+, Perkin-Elmer).

The CO_2 absorption method has been used since the late 1980s for the analysis of different kinds of samples with both high- and low-level activity, and with a wide range of applications. First developed for groundwater research, it was then employed for analysis of environmental and archaeological samples. The CO_2 analyzed is derived from both acidification of carbonates (shells, corals, carbonates) and combustion of organic samples (wood, charcoals, peat) (e.g. Qureshi et al. 1989; Leaney et al. 1994; Nair et al. 1995). The direct absorption method of ^{14}C dating has been improved during the last decades so that standard errors and reliability of dates from the past 30,000 yr are now similar to the errors of other conventional radiometric techniques (Vita-Finzi and Leaney 2006). Recently, the method has been successfully used for evaluation of ^{14}C activities in atmospheric and biological samples (Bronić 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; Norton and Devlin 2006).

Several experimental arrangements have been proposed by many authors and, as a general rule, they are all based on a system for the production or collection of CO_2, followed by transfer, into an absorbing medium. The main obstacle is usually setting up an efficient system capable of quantitative CO_2 collection within the shortest possible processing time. To achieve this goal, some authors report the use of an airtight system under an inert atmosphere plus closed-loop recirculation of gases, or the use of plastic bags or bladders (Leaney et al. 1994; Molnár et al. 2006; Varlam et al. 2007).

Several papers have already reported the potential advantages of the CO_2 cocktail–LSC method (Noakes et al. 2006; Norton and Devlin 2006) in terms of time, cost, safety, and affordability. Nevertheless, due to some unresolved drawbacks, i.e. higher background and lower sensitivity and accuracy, so far it has not been extensively applied despite its remarkable potential. It has even been removed from the latest version of the standard method (ASTM International 2012). This exclusion could also be related to the fact that this method is widely used in analytical activities involving ^{14}C-enriched matrices (i.e. nuclear material characterization and nuclear power plant monitoring activities), and so very little effort has been devoted to lowering the accuracy limits because it is not a priority in these application fields. For this reason, it is strongly believed that further experimental studies are needed to evaluate the applicability of the method, and possible improvements of the technique, to further the potential of the method for biobased analysis.

On the basis of these considerations, we report the results of an investigation including:

- Optimization of experimental conditions in order to minimize the experimental artifacts during the CO_2 absorption process;
- Selection of an efficient counting cocktail for ^{14}C LSC analysis;
- Standardization of a suitable experimental protocol compatible with ASTM D6866-11.

MATERIALS AND METHODS

Experimental Apparatus

The experimental apparatus is composed of a 5-L flask equipped with an inlet for gas storage, 4 cryogenic traps with different volume capacities (three 600-mL traps plus one 100-mL trap), a vacuum pump inlet, pressure transducer, and vacuum gauges, and a vial containing the absorbing solution (Figure 1). The flask collects and stores the CO_2 samples to be analyzed in sufficient amounts to ensure replicates of the analyses. The cryogenic traps in the system are designed to contain an excess amount of CO_2 to ensure a quantitative reaction with the absorbent present in the vial. The use of several stopcocks at different points in the system permits different volume capacities depending on the amount of sample available and the progress of the reaction (about 2, 1.3, or 0.1 L, depending on the number of traps used).

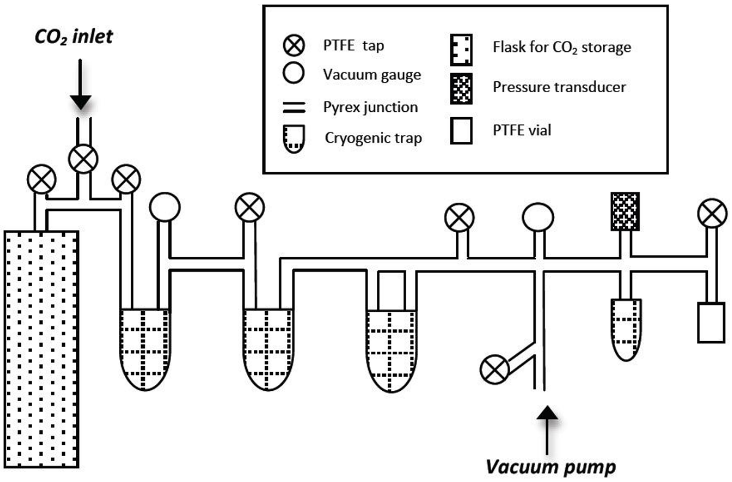

Figure 1 Equipment for the CO_2 direct absorption method composed of a flask for gas storage, 4 cryogenic traps able to store different amounts of CO_2, vacuum gauge to check the cleaning of the system, pressure transducer for real-time monitoring of the reaction, and a vial containing the absorbing solution.

With respect to conventional setups used in this field, the system was herein improved by adding a pressure transducer for monitoring the progress of the reaction in real time. A second upgrade is represented by the new CO_2 absorption cell. In particular, the vial was designed to fulfill the following requisites:

1. An optimized, air-tight fitting to the gas line setup by means of an internal thread so that it can be directly screwed to the end junction of the line;
2. Recovery of the vial after gas processing without any liquid transfer, i.e. LSC is carried out directly in the cell;
3. Use of PTFE for its fabrication in order to minimize instrumental background during LSC analysis.

The vial contains an absorbing solution to chemically trap the CO_2. The typical sorbent, namely Carbosorb E, is according to manufacturer's specifications a 3-methoxypropylamine, but no information about the degree of purity of the substance is provided. For these experiments, an equivalent reactive supplied by Acros Organics (>95% by weight) was used, resulting in better reliability of the product components as well as lower cost.

Experimental Protocol

The procedure for ^{14}C analysis first requires preparing and connecting the vial to the end junction of the system. The PTFE vial is first filled with the absorbant (8 mL 3-methoxy-propyl-amine) and tightly closed under an inert atmosphere (argon) in order to minimize the possible risk of contamination by atmospheric CO_2.

The gaseous sample (e.g. CO_2 derived from acid hydrolysis of carbonates or oxidative combustion of organic samples) is collected into the system previously evacuated. A sufficient amount of CO_2, depending on the sample size, is then transferred and frozen by liquid nitrogen in the cryogenic traps to reach a pressure in the range of 1–1.4 bar, and finally it is allowed to sublime and react with the amine. The system has been designed with an overall capacity (~7 L including the storage flask, or ~2 L with only the cryogenic traps and junctions) able to contain an excess of gas to ensure the complete conversion of CO_2 and amine into the carbamate at low pressure, avoiding security risks. The conversion of the amine into carbamate is a well-known exothermic process. Next, the vial is placed in an ice bath to reach the reaction equilibrium as well as to limit the loss of the volatile absorbant. The pressure transducers allow real-time monitoring of the reaction's progress. Amine saturation is achieved when the CO_2 pressure is stable. If required, that is, the CO_2 pressure still decreases, more transfer cycles from the storage flask can be performed. The absorption process takes about 15–20 min per sample.

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 complete achievement of high-level saturation (greater than 80%) ensures easier and faster handling of the vial without requiring the use of a glove-box, as the risk of contamination is presumably very low because the reactive is mostly converted in a stable form.

The sample of freshly formed carbamate in the PTFE vial is then combined with 10 mL of scintillator (Permafluor E+, PerkinElmer) and mixed with 2 mL of methanol (Carlo Erba, analytical grade) to prevent the risk of phase separation at a saturation level higher than 80%. The vial is then shaken and eventually sonicated to complete homogenization. The overall time required for each sample preparation is about 1 hr. The sample is finally counted for ^{14}C content determination by the Quantulus™ 1220 (PerkinElmer). The vial is stored for a few hours before counting in order to prevent chemiluminescence interference during ^{14}C counting.

Optimization of the Counting Conditions

The ^{14}C window was set between channels 100 and 380 as determined through the figure of merit of a standard spectrum equal to 1026. The total counting time was 600–1000 min to achieve statistically significant data. The background of the instrument and the counting efficiency were determined using as standards the CO_2 derived from acid hydrolysis of Carrara marble (background standard) and from the oxidative combustion of a certified reference material (IAEA C6 sucrose, modern standard). The preparation of the CO_2 samples used for this calibration was performed using the system already working in this lab for benzene synthesis and LSC (Magnani et al. 2006). The CO_2 produced was then transferred and collected in the absorption system previously described.

RESULTS AND DISCUSSION

The new setup has been characterized in terms of background, efficiency, minimum detectable activity, and maximum detectable age; the obtained results are summarized in Table 1. The new absorbent investigated shows performance comparable with the conventionally used Carbosorb E. The average amount of CO_2 absorbed is 4 mM/mL amine corresponding to an average saturation level of 80% according to Carbosorb E specifications and scientific literature (e.g. Horvatinčić et al. 2004; Molnár et al. 2006).

Table 1 Features of the new system and methodology (the minimum detectable activity [MDA] is calculated according to the method detailed by L'Annunziata [2003]; the maximum age is calculated according to the convention proposed by Stuiver and Polach [1977]).

Standard – ANU sucrose (IAEA C-6)			Background – Carrara marble		
AON (cpm/gC)	pMC (%)	Efficiency (%)	CPM (100-380)	MDA (Bq/gC–pMC)	Maximum age (yr BP)
13.5 ± 0.1	151 ± 2	65 ± 1	1.42 ± 0.09	0.02–8	36,000

The background count rate was found to be 1.42 ± 0.09 cpm (average value of 3 replicates in 3 different PTFE vials). As expected (Noakes et al. 2006), this value is considerably higher than the typical background obtained with benzene synthesis, which corresponds to 0.15 cpm/g C usually recorded in our laboratory. However, the count rate is comparable or slightly lower than most values reported by other authors with different cocktail compositions (Figure 2). Though the use of PTFE vials has already been investigated and routinely applied to benzene synthesis, there are only a few reports related to the direct absorption method (Nair et al. 1995). To better evaluate the effect of the vial material on the background count rate, we tested different kinds of materials (PTFE, PE, and low-^{40}K glass vials) filled with the same cocktail composition (8 mL 3-methoxy-propyl-amine + 2 mL methanol + 10 mL Permafluor E+) used to determine the system "blank." The use of PTFE showed the best performance and resulted in a significant reduction in background counting (cpm), up to 40% in comparison to the low-^{40}K glass vials (count rate of 1.48[0.04] in spite of 2.49[0.07] in the same region of interest). The PE vials displayed a count rate statistically comparable to the PTFE vials (count rate of 1.53[0.06]); however, their use is not recommended for this application due to the corrosive action of the amine on the container.

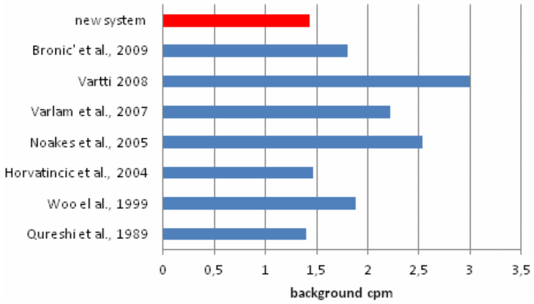

Figure 2 Comparison between cpm backgrounds measured by different authors.

The most relevant advantage of the new PTFE vial design, however, is its versatile use both for sample processing and ^{14}C counting. This improvement minimizes the risk of sample loss during transfers and the risk of sample contamination from ambient CO_2. The comparison between the blank counting value, referred only to the cocktail composition, and the background counting value, referred to the entire process, suggests that there is no relevant contamination during the preparation, process reaction, and handling of the CO_2 cocktail–PTFE vial (Figure 3).

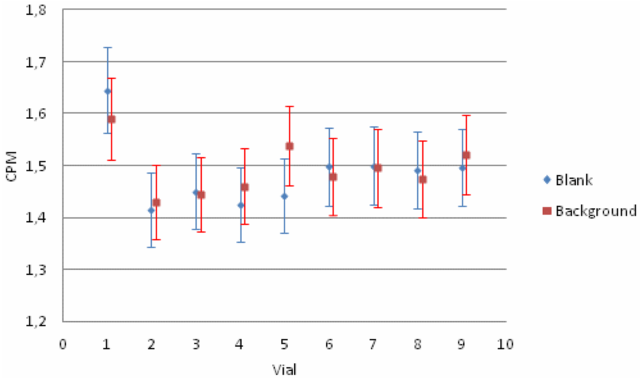

Figure 3 Comparison between blank and background count rate in different vials (5% error bars).

The minimum detectable activity calculated according to the method detailed by L'Annunziata (2003) is 0.02 Bq/g C for a counting time of about 600 min, compatible with routine measurements, and corresponding to a minimum pMC detectable of 8%. The associated maximum detectable age (calculated as proposed by Stuiver and Polach 1977) results in 36,000 yr BP. The count rate of the ^{14}C calibration standard (IAEA-C6) is 13.27 cpm/g C (normalized to $\delta^{13}C = -25‰$ with respect to PDB) and the counting efficiency was evaluated to be 65%. This value is in agreement with other independent work (Varlam et al. 2007; Bronić et al. 2009) and is acceptable according to ASTM D6866-11.

As previously mentioned, the addition of a small amount of methanol to the cocktail (as suggested by LSC in Practice Radio-Carbon Dioxide [$^{14}CO_2$] Trapping and Counting – PerkinElmer Application Note) ensures the stability of the liquid solution, as required by the beta counter technique, and avoids the risk of phase separation between the amine converted to carbamate and the scintillator. In order to check the stability of the solution, a standard sample with a high CO_2 content was counted for a long time in a sequential mode, i.e. 99 subsequent cycles of 60 min each resulting in a total counting time of about 5800 min. The data collected show the stability and the reliability of the cocktail even after several days (mean value and standard deviation equal to 6.6[0.3] for CPM and 683[2] for SQP). Typical spectra of modern and background samples obtained with the direct absorption method and the system described are shown in Figure 4.

CONCLUSION

An innovative method was tested for the direct absorption of CO_2. It is characterized by a PTFE vial and a system for absorption that provide a lower background rate and improvement in the minimum detectable activity and the maximum detectable age. The developed method is simple, quick, and cost-effective. In addition, it resulted in a counting efficiency that is acceptable according to ASTM D6866-11, thus widening the possible field of application for the direct CO_2 absorption method.

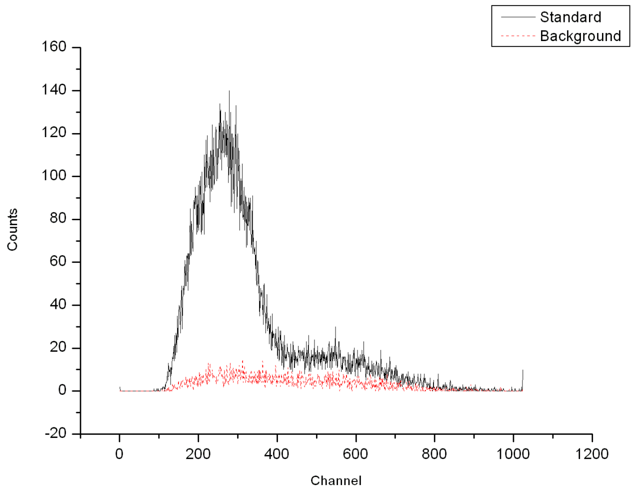

Figure 4 Typical ^{14}C spectra of standard (ANU sucrose) and background (Carrara marble) in LSC obtained with the CO_2 cocktail method.

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