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UTILIZATION OF AMMONIUM HYDROXIDE COMPOUND AS CARBOSORB FOR MEASUREMENT OF CARBON-14 IN DETERMINATION AGE OF CORAL REEF SAMPLE FROM SPERMONDE ISLANDS

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ABSTRACT

Utilization Of Ammonium Hydroxide Compound As Carbosorb For Measurement Of Carbon-14 In Determination Age Of Coral Reef Sample has been performed. The objective of this research is to Determine the age of Coral Sample of Spermonde Islands through Activity Measurements of carbon-14 with LSC (Liquid Scintillation Counting) method. Coral sample were taken from around Langkai Island. The steps of this research are: Sample preparation, CO_2 absorption with solution of MEA, DEA and TEA and measurement of carbon-14 activity using Liquid Scintillation Counter (LSC) Hidex 300 SL. Absorption CO_2 using ammonium hydroxide. The specific activity of coral sample using carbosorb ammonium hydroxide was 14.43 ± 1,2 DPM/g C. The age of coral sample calculated from the specific activity using carbosorb ammonium hydroxide was 484.63 ± 54 years.
Keywords : LSC (Liquid Scintilation Counter), Carbon-14, CO_2 Absorption, Ammonium hydroxide, Langkai Island

INTRODUCTION

Spermonde Islands is one of the most important area in South Sulawesi. Spermonde Islands identified ± 400,000 ha. Coral reefs are found in the waters of Indonesia are more than 60,000 km^2 and most of them found from eastern to western Indonesia. There are 350 species of coral found in Indonesia, 250 species of which found in Spermonde Islands the reef area of 150 km^2. Spermonde Islands coral diversity levels are quite high because there are 78 genera and sub-genera, with 262 species of a total coral judging from the level of deployment, approximately 80% -87% of the region, the outer reef (Coremap, 2003).

Determination of age of the coral reefs die in a sea also has enormous benefits in studying the geography of the sea coral origin such as samples to trace and study the establishment of a sector in coastal rock formations. Besides the determination of age, coral reefs can also be used to determine the apparent radiocarbon age of the sea (Yuliati and Akhadi, 2005).

Arman et all (2013) determined age of the coral reefs and growth rate of reef to determine the characteristics of the water such as an increase in sea surface temperatures, one of which caused by the El-Nino in the Thousand Islands. Characteristics of the waters can be identified through a decrease in the rate of linear growth of coral reefs, especially in times of El-nino on a large scale as in 1997-1998 and 1982-1983. The decline in the rate of linear growth is also due to factors occurring water conditions on a small scale (local) as a result of increased levels of pollutants, nutrients and sedimentation.

Determination age of the coral reefs can be known through radiocarbon dating method. This method is based on the calculation of the ^{14}C activity was

contained in a carbon sample. The value of this activity is then converted into the age when compared with the reference standard modern. ^{14}C (radiocarbon) is produced in the atmosphere produced with the reaction between cosmic radiation and nitrogen, forming ^{14}C. When a subsystem (trees, sea shells and others) isolated from the global system (eg trees are cut, or dead and buried in the ground) and then no more radiocarbon is added to it, then the activities of the radiocarbon (^{14}C in a number of subsystems or footage) start reduced in accordance with the law of radioactive decay (Faisal, 2009).

The last few years, scientists have developed a liquid scintillation counting method for the measurement of total α and β in environmental samples, because existing methods (electrodeposition method) is quite complicated. Liquid scintillation counting method is now not only used for the counting of low-energy β radiation, but can be used also for counting of α and β total. This method is known as LSC (Liquid scintillation Counting). Advantages compared with the previous method is a liquid preparation facilitate sample dissolved homogeneously, so there is no effect of self-absorption. This method can detect ^{3}H and ^{14}C, and can determine α and β the total at once, thereby saving time (Tjahaja and Mutiah, 2000).

Method of age determination using $_{14}C$ during chopping is done by liquid scintillation counter with C_6H_6, chopping C in the form of graphite with AMS (Accelerator Mass Spectrometry) and chopping CH_4 with Mini Gas Proportional Spectrometry. These methods are rarely used in the determination of age because of the cost of equipment and materials to repair the sample is very expensive. Sample preparation is quite complicated, long and requires consideration of adequate technical skills so as to study hydrology especially uneconomical and inefficient, because only one sample can be analyzed daily. The last two decades have started to develop CO_2 absorption method is better than previous methods (Satrio and Abidin, 2007).

Yarianto et all (2001) used liquid scintillation counter to determine the optimum conditions for the determination of the radioactivity of ^{32}P labeled insect pests. Panggabean (2002) reported the adaptation of the method of analysis of ^{14}C in sea water using NaOH absorber by means of LSC. In 2010 Suyarso reported past changes in sea level by the age of the fossil shells with CO_2 absorption method using a liquid scintillation counter. Satria et al (2012) determined the age of the Lapindo mud water and mountain stalactites kidul with CO_2 absorption method using a liquid scintillation counter. Therefore, in this study will be conducted to determine the age of the coral reefs in the maritime Spermonde through measurements of ^{14}C activity by LSC method using NH_4OH carbosorb.

MATERIAL AND METHODS

Materials

The materials of this study was 30% H_2O_2, $HClO_4$ 1 N, 1 N NaOH, ethanolamine, N_2 gas HP (High Purity), 10% HCl, $AgNO_3$, silica gel, marble, scintillator aqualight LLT, filter paper, distilled water and coral reefs .

Apparatus

Preparation tool in the form of round-bottom flask, impinger, funnel, absorption column, glass cup, mortar, gloves, oven, hammer and tools glasses commonly used in laboratories as well as β radiation count tool of carbon-14 sample is LSC Hidex 300 SL.

Sampling

Coral sample taken at seawater near one of the islands in the Spermonde Archipelago, which is in Langkai Island at a depth about 4-5 m. Langkai Island

located on coordinate S: 05° 01' 47,055" E: 119° 05' 50,272".

Phisical and Chemical Cleaning

Cleaning methods are designed to remove contaminating carbon sources that accumulate both while the specimen is on the sea floor and while it is stored on land after collection. Water rinses and scrubbing with a brush remove sediment from inside the coral and between the septa. Samples are then immersed in a 1:1 mixture of 30% H_2O_2 and 1N NaOH and ultrasonicated for 15 minutes. However, this process often leaves a brownish/orange organic stain on the $CaCO_3$. Quick dips (30 seconds to 2 minutes) in a 1:1 mixture of 30% H_2O_2 and 1N $HClO_4$ effectively remove this stain. After the dilute perchloric step, samples are rinsed thoroughly with clean distilled water. For the second acid wash, pre-weighed samples are dipped into 6N HCl for 15–60 seconds followed by rinses in two separate beakers of distilled H_2O. After drying for several minutes in a 60 °C oven, the samples are cooled and reweighed to determine the percent of sample removed. Samples are then crushed in an agate mortar and pestle to facilitate dissolution in the reaction flasks.[1]

Carbon Dioxide Absorption

Dried coral were transferred to flask that connected to a separation funnel as hydrochloric acid reservoir. Prior to carbon dioxide absorption, the nitrogen gas was streamed along the system. Solution of 10 % HCl was added by drops to the sample until bubles formed (Fig.1).Gas is channeled into an impinger contains 40 mL ammonium hydroxide as carbosorb after passed acid trap and water trap. The process was stopped when the gas not formed by adding the hydrochloric acid. Concentration of CO_2 absorbed was quantified from the difference of weight before and after absorption process

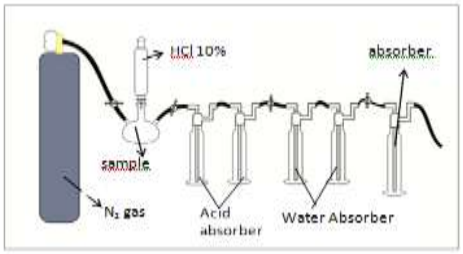

Figure 1. Design of absorption system of carbon dioxide from coral sample

The same method is used to absorb CO_2 from Marble for use in the measurement of the Background

Determination of Total Carbon

$(NH_4)_2CO_3$ dissolved pipetted in Erlenmeyer 10 mL to titration with 5 M HCl solution after the addition of a few drops of indicator MO until the color changes from brown to pink. Furthermore, pipette 10 ml of $(NH_4)_2CO_3$ into a beaker for added $BaCl_2$ 10% solution until be precipitation (saturated). Subsequently, the precipitate and the filtrate was separated used filtered, then the filtrate was pipetted into Erlenmeyer 10 mL for titrated with 5 M HCl solution with the addition of a few drops of indicator PP until the color changes from purple to clear.

Carbon-14 Counting

Approximately 8 mL of sample or background mixture with 12 mL scintillator in 20 mL vial. The mixture was homogenated by shaking and saved from light exposure, and then lied on 20 mL vial plate tray. Counting the sample as protocol LSC Hidex 300 SL and it was counted at 5-240 minutes in range.

RESULT AND DISCUSSION

Phisical and Chemical Cleaning

Coral sampel that have been physically and chemically cleaned looked clean and white. The chemical cleaning removed impurities and carbon source on the surface up to 8,63 %. The result of these experiments are not much different from the result of deep-sea coral sample

cleanup was done by Adkins et al. [1] and Maming et al.[6] The missing part of the sample is a natural contaminant that accumulates over the coral reef waters and dissolved matrix surface.

Counting Carbon-14

The results of measurements of ^{14}C activity measured on the instrument is expressed in units of Count Per Minute (CPM) which shows the number of β particles produced from ^{14}C in coral sample in every minute, and the activity of coral sample is expressed in units Disintegration Per Minute (DPM) which shows the actual number of atoms in the ^{14}C decays coral samples in every minute. The relationship between the value of DPM and the value CPM is expressed as a form of efficiency in units of counting which stated Triple Double Coincidence Ratio (TDCR).

Measurement of background was done by the CO_2 absorption using marble as a source of CO_2 background. Marble is a carbon source with old age that is considered to contain carbon-14 with very low activity. Determination of the optimum time of counting was performed to determine the best time and the resulting DPM value and TDCR value stable as a sign that the sample counting process running optimally. In 90-240 minutes, activity values of ^{14}C ranging achieve stability. The optimum time of counting sample and background are determined based on the figure 2. The optimum time of counting is 120 minutes for sample and optimum time of counting is 60 minutes for background.

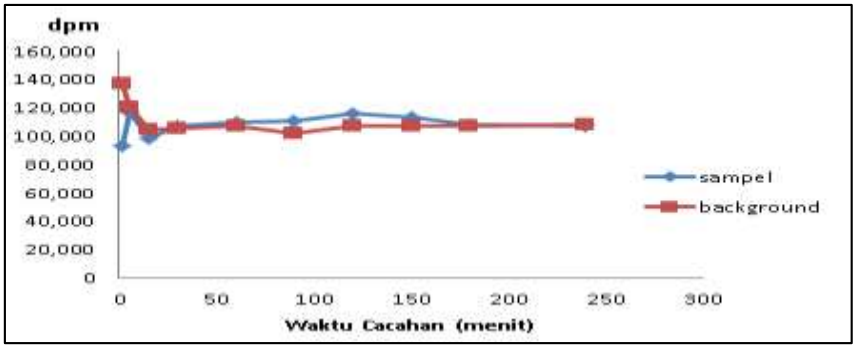

Figure 2. Determination of Counting Time Optimum Sample and Background Of Coral Reef

Determination of specific activity of the sample of coral reefs can known based counting from sample and background at the optimum time respectively 120 and 60 minutes. The counting is done as much as 7 times repetition, in order to obtain the average activity of the sample and the background can be seen in Table 2. The average activity data is then used to determine the value of the specific activity of samples of coral reefs.

Table 2. Activity of ^{14}C Sample and Background

Sample		**Background**	
DPM	**TDCR**	**DPM**	**TDCR**
108,030	0,604	104,690	0,602
107,630	0,588	104,320	0,604
107,310	0,603	103,370	0,605
106,990	0,603	103,320	0,596
106,770	0,600	102,800	0,607
106,500	0,606	102,660	0,609
106,030	0,604	101,920	0,610

The specific activity of samples of coral reefs can be determined from the difference between the results of Disintegration Per Minute (DPM) of sample and the results of Disintegration Per Minute (DPM) background divided by the total content of carbon in 8 mL of sample were mixed with 12 ml of scintillator. Determination of total carbon contained in the coral reef sample titration method and gravimetric method. Both methods are very supportive in this study. Total carbon mass obtained on samples of coral reefs are shown in Table 3. The value of the specific activity is indicated by DPM units per unit mass. Specific activity data samples of coral reefs are shown in Table 3. The value of the specific activity (As) shows the number of atoms of 14C that decays every minute in one gram of carbon element.

Table 3. The Specific Activity (As) of Coral Reef Sample from Langkai Island

DPMs	DPMb	DPM	C-total (g)	As (DPM/gC)	As C-14 life
107.037	103.297	3,740	0,2592	14,43 ± 1,2	15,30 ± 0,1

Age determination of coral sample is determined based on the specific activities that have been obtained previously. The age of coral sample calculated from the specific activity using ammonium hydroxide as carbosorb was 484.63 ± 54 years.

CONCLUSION

The specific activity of coral sample using ammonium hydroxide as carbosorb was 14.43 ± 1,2 DPM/g C. The age of coral sample calculated from the specific activity using ammonium hydroxide as carbosorb was 484.63 ± 54 years.

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