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UTILIZATION OF METHYLAMINE COMPOUND AS CO_2 ABSORBENTS FOR MEASUREMENT OF CARBON-14 IN CORAL REEF SAMPLE FROM SPERMONDE ISLANDS

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ABSTRACT

Utilization of methylamine as CO_2 absorbent to measure carbon-14 activity of coral sample has been done. The objective of this research is to Determine the age of Coral Sample through Activity Measurements of carbon-14 with LSC (Liquid Scintillation Counting) method. Sample were taken from Langkai Island which is far from human activities. Sample preparation includes physical and chemical leaching to produce a clean white sample. Carbon in the sample was released as CO_2 by reaction with HCl 10 % and than absorbed by methylamine yield carbamate compound. Absorbed carbon in 1 mL absorber was 0,044 g from the results of weight reduction before and after absorption. The specific activity of the coral sample was 14.56 DPM/g C. Age of the coral sample based on the specific activity was 408.48 ± 43.69 years.

Keywords : LSC (Liquid Scintilation Counter), Carbon-14, CO_2 Absorption, Langkai Island

INTRODUCTION

Coral reef ecosystems in tropical sea floor built primarily by marine organisms producing limestone ($CaCO_3$) which hermatifik corals that live in symbiosis mutualism with zooxanthellae, a type of unicellular algae found in the coral polyps and perform photosynthesis. In symbiosis, zooxanthellae produce oxygen and organic compounds through photosynthesis which will be used by corals, while the corals produce inorganic components such as nitrate, phosphate, and carbon dioxide for the zooxanthellae living purposes. Byproducts of this activity is calcium carbonate (Wahyu, 2011).

The level of diversity of coral on the Spermonde island fairly high because there are 78 genera and sub-genera, and 262 species. Several species of coral reefs and other marine organisms in Spermonde island is an endangered species (Moll, 1983 in Jompa, 2005). On the other hand the study of the genesis of the Spermonde as coral-based island remains a mystery, especially to uncover information about when and how the formation of the island.

The age of a sample can be determined by measuring the radioactivity of an element contained in the sample. One of the radioactive elements that can be measured are isotopes of carbon, ie, carbon-14 (^{14}C). The carbon isotope, ^{14}C, emits beta particles (β) and will decay over a period of 5730 years into a stable ^{14}N (Clark and Fritz, 1997). ^{14}C element reacts with oxygen yield carbon dioxide which would then be absorbed by plants for photosynthesis. Furthermore, ^{14}C will spread to all living beings through food cycle. The existence of ^{14}C in organic materials is the basis of radiocarbon dating to estimate the age of the archeology, geology, and hydrology samples.

Analysis of ^{14}C in the sample can be measured by converting carbon into a gas

such as carbon dioxide which is then inserted into a detector that is sensitive to beta rays (Hidayat, 2008). The last few years scientists have developed a radiation instrumentation for measuring very low radiation intensity. The instrument is specially designed for count a very low radiation. The radiation instrument is a liquid scintillation counter (LSC) (Tjahaja and Mutia, 2000).

There are two methods of pre-treatment samples in radiocarbon analysis using the LSC. The first method is synthesis of benzene and acetylene, where samples are count using gas scintillation counter in the form of acetylene gas or liquid scintillation counter in the form benzene. The second method is an absorption method where carbon absorbed by the absorber in the form of CO_2. Absorption method is more effective because safer, easier, and short process compared with synthesis method. Primary amine is the most effective absorbent compound for use as an absorber, this is because the primary amine compound capable of absorbing CO_2 in large capacity and has a high selectivity for CO_2 (Kim and Kim, 2004), (Yu et al, 2012).

Based on the research that has been done by Satrio and Sidauruk, 2009, the primary amine compound 2-metoksietilamin is very relevant absorber. The compound 2-metoksietilamin count values are relatively stable in the blank and standard sample. However these compounds are difficult to obtain in the market and has a high price so that we need alternative absorber which is more economical and easy to obtain. One of the primary amine compounds which common, readily available, and more economical is methylamine compounds. Based on this problem we conducted this study.

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

Sample were obtained from Langkai island in Spermonde archipelago, South Sulawesi, in 4-5 meter deep from water surface. Sampling of coral reefs aided by SCUBA drivers with tools such as drill and hammer.

Sample cleaning

Sample cleaned through two stages which is physical leaching and chemical leaching. Samples of coral reefs washed in flowing water with a brush and then rinsed with distilled water. After physical leaching, the samples were dried. Samples were soaked with a mixture of H_2O_2 30% and NaOH 1 N in the ratio 1:1 and ultrasoniced for 10 minutes and then rinsed with distilled water. Subsequently the samples were stored back into the mix of H_2O_2 30% and $HClO_4$ 1% with a ratio of 1:1 and then rinsed again with distilled water. The samples then immersed in 10 mL of HCl 10% for 15-60 seconds and rinsed again with distilled water. Samples were spotless white after the chemical leaching process completed. The samples then dried in an oven at 105°C until dry.

CO_2 Absorption

A total of 40 g crushed sample put in a flask and assembled as shown in Figure 1. After that, the circuit was saturated with N_2 gas to remove CO_2 contaminants in the circuit. Once saturated, the N_2 gas flow was stopped and then the sample was treated with 10% HCl yield CO_2 gas. The CO_2 gas than passed through the acid, water, and CO_2 absorbent column containing methylamine compounds. The amount of CO_2 absorbed is determined based on the weight before and after absorption. The same method is applied on a marble background absorption process.

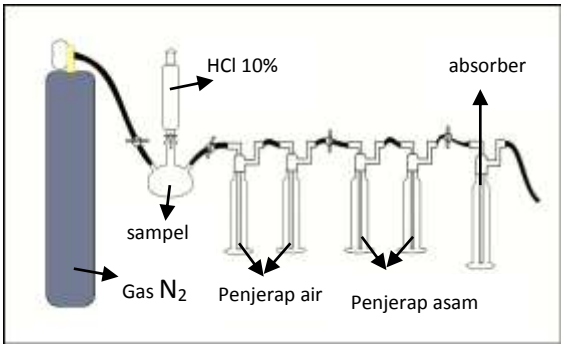

Figure 1. CO_2 absorption circuit

^{14}C Counting

A total of 8 mL of sample was mixed with 12 mL sintillator into 20 mL vials. The mixture was shaken until homogeneous and kept from light. Vial is then placed on a LSC Hidex 300 SL tray and the counting procces strated.

Age Determination Of The Coral Reefs

Age of coral reefs can be calculated using radiocarbon decay rate equation :

$$t = \frac{t_{1/2}}{ln\,2} ln \frac{A_0}{A}$$

A = Radioactivity of ^{14}C isotope in the sample

A_o = Radioactivity isotope ^{14}C when the sample was still alive (15,3 DPM/g C)

$t_{1/2}$ = ^{14}C half life (5730 years)

Ln 2 = 0,693

RESULTS AND DISCUSSION

Sampling

Samples were taken on the Langkai island which is the outer islands of the Spermonde archipelago with coordinate S: 05º 01' 47,055" E: 119º 05' 50,272". In addition, the condition of coral reefs on the island is relatively better than other islands, because Langkai island far from human activities

Figure 2. Coral Sample from Langkai island.

Sample Cleaning

The aim of sample cleaning was to eliminate organic and inorganic contaminant. Washed sample is spotless white and look cleaner than before. There are differences in the weight of the sample before and after washing. This is due to the loss of impurities attached to the surface of the sample. The weight of the sample before washing is of 276.505 g and after washing reduced to 252.653 g. From these data it can be seen that the weight lost after the washing process is carried out at 8.63%.

CO_2 Absorption

CO_2 gas produced from the reaction between the sample and HCl will be absorbed by methylamine forming carbamate compounds based on the reaction that shown in figure 3.

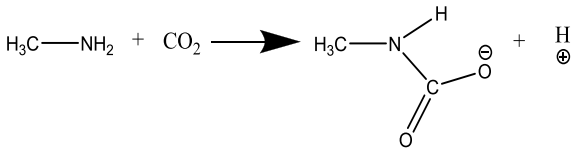

Figure 3. Reaction beetwen methylamine and CO_2

The exothermic reaction takes place in this raction characterized by increasing temperature absorber solution. Absorption process is stopped when the solution was saturated. The temperature was gradually returned to room temperature in a saturated condition. Total carbon absorbed is calculated based on the difference in weight before and after the absorption process. The amount of CO_2 absorbed in 1 mL of methylamine was 0.044 g. Methylamine absorption efficiency of 8.7% is obtained from the quotient of the total CO_2 absorbed in 40 mL of methylamine and CO_2 molecule relative.

^{14}C Counting

Sample were counted untill the optimum time of sample count obtained. Optimum time count results can be seen in Figure 4. The results of measurements of carbon-14 activity by LSC Hidex 300 SL form of count per minute (CPM) and the value of disintegration per minute (DPM).

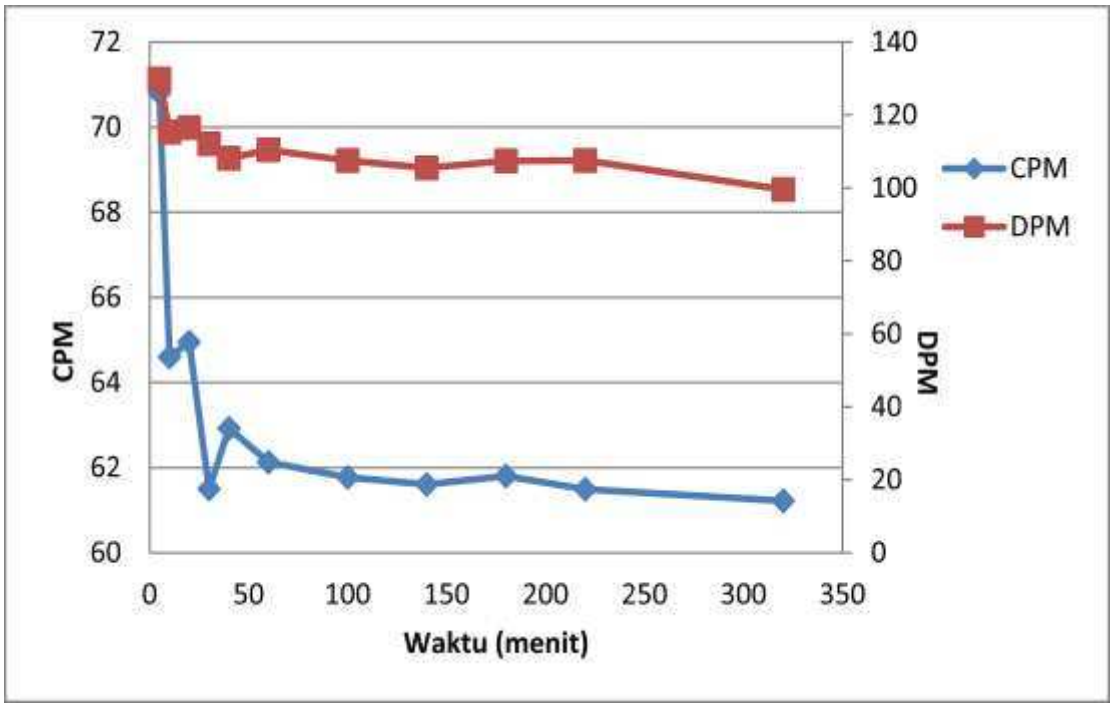

Figure 4. Optimum time count results

The picture shown optimum time counting were 140 minutes. ^{14}C activity fluctuating values caused by the effects of chemical glow (chemiluminescence) when counting takes place and the phase instability between the scintillator and carbamate solution at the beginning of the counting process. Phase instability caused by the effects of quenhcing. After the optimum time obtained, counting continued to determine the average value of counts at the optimum time. The same thing is done in the background. For background measurement, marble were used as a source of carbon. Marble is a carbon source with a very old age so that it contains carbon-14 with very low activity. Counting results for the determination of

the average value of counts can be seen in Table 1.

Based on the data obtained, specific activity of coral samples was 14.56. The age of coral sample by using methylamine as the absorber was 408.48 ± 43.69 years. The specific activity can be calculated by dividing the value of DPM correction. with the total carbon sequestered in 8 mL of sample. While DPM correction is DPMS minus DPMB. The specific activity obtained is worth 14.56 DPM / gC.

Tabel 1. Counting results for the determination of the average value of counts

Time (minute)	CPM		DPM	
	CPM s	CPM b	DPM s	DPM b
140	65,930	59,710	107,400	105,670
	63,370	59,370	102,860	102,750
	65,129	59,730	105,480	101,430
	63,920	60,200	103,780	103,270
	64,530	59,600	103,670	103,000
average	64,576	59,722	104,638	103,224

CPM = *Count Per Minute* DPM = *Disintegration Per Minute*

Determination of Coral Reef's Age

Specific activity values obtained were then put into the equation formula,

$$t = \frac{t_{1/2}}{ln\,2} ln \frac{A_0}{A}$$

from the calculation, the age of the samples obtained coral reefs are worth 408.48 ± 43.69 years.

CONCLUSION

The specific activity of the sample was 14.56 DPM / g C and age of the samples obtained was 408.48 ± 43.69 years. Methylamine compounds can be used as an absorber of CO_2 with an efficiency of 8.7%.

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