



## DETERMINATION OF AGE OF CORAL REEFS ON PANIKIANG ISLAND, BARRU DISTRICT, SPERMONDE ISLANDS THROUGH MEASUREMENT ACTIVITY $^{14}\text{C}$ USING LSC (*LIQUID SCINTILLATION COUNTING*) METHOD

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### ABSTRACT

Determination Of Age Of Coral Reefs On Panikiang Island, Barru District, Spermonde Islands Through Measurement Activity  $^{14}\text{C}$  Using LSC (Liquid Scintillation Counting) Method. This research was using a sample of coral reefs taken from the Panikiang Island, Barru, Spermonde Islands. This research has been carried out by using sample preparation with physic and chemical. Sample preparation was done physically and chemically. Chemical preparation was carried out by using a mixture of NaOH with 30%  $\text{H}_2\text{O}_2$  followed by a mixture of  $\text{HClO}_4$  with 30%  $\text{H}_2\text{O}_2$ , and finally with HCl solution to produce a clean sample with a weight reduction of 7.94%. Absorption of  $\text{CO}_2$  through reaction with HCl 10% and  $\text{NH}_4\text{OH}$  as *Carbosorb* produced  $\text{K}_2\text{CO}_3$ . The total carbon in the sample solution is 0.2496 gram obtained through titration method. Radiocarbon dating method based on the measurement of the specific activity of the samples obtained from the results of counts LSC (*Liquid Scintillation Counter*) Hidex 300 SL. The specific activity of coral sample is  $14.68 \pm 4.04$  DPM/gC. Age of coral sample which were calculated from the specific activity were  $342.04 \pm 37.66$  years.

**Keywords:** Specific Activity, Coral Reef, LSC, Radiocarbon dating

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### 1. INTRODUCTION

The Spermonde Islands are one of the most important marine areas in South Sulawesi. The Spermonde Islands identified  $\pm 400,000$  ha. The area of coral reefs are found in the waters of Indonesia are more than  $60,000$   $\text{km}^2$  and most of them found from eastern to western Indonesia. There are 350 species of coral found in Indonesia, 250 species of them are found in Spermonde Islands in a  $150$   $\text{km}^2$  coral reef area. The Spermonde Islands coral diversity levels are quite high

because there are 78 genera and sub-genera, with a total of 262 species. Viewed from the level of coral spread, around 80% -87% are found in the outermost reef areas.

Determination of age of dead coral reefs in a sea also has enormous benefits in studying the geographic 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 [1].

Determined the 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 Seribu Island. Characteristics of the waters can be identified through a decrease in the rate of linear growth of coral reefs, when El-Nino occurs on a large scale as in 1997-1998 and 1982-1983. The decline in the rate of linear growth is also caused by factors of water condition that occur on a small scale (local) as a result of increased levels of pollutants, nutrients and sedimentation [2].

Determination age of the coral reefs can be known by measuring the radioactivity of the elements in the sample and by measuring the age of the coral, information can be used to trace and study rock formation on a coast and on the earth's surface, knowing the age of marine coral samples, so that the history of the formation of the earth can be expressed more clearly with the support of accurate data [1].

The last few years, scientists have developed a liquid scintillation counting method for the measurement of total  $\alpha$  and  $\beta$  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  $\beta$  radiation, but can be used also for counting of  $\alpha$  and  $\beta$  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  $^3\text{H}$  and  $^{14}\text{C}$  can also determine  $\alpha$  and  $\beta$  the total at once, thereby saving time [3].

Method of age determination using  $^{14}\text{C}$  during chopping is done by liquid scintillation counter with  $\text{C}_6\text{H}_6$ , chopping C in the form of graphite with AMS (Accelerator Mass Spectrometry) and chopping  $\text{CH}_4$  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  $\text{CO}_2$  absorption method is better than previous methods [4].

The application of the LSC (Liquid Scintillation Counting) method through the measurement of  $^{14}\text{C}$  activity in determining the age of a material has played an important role, not only in the discovery of the age of ancient objects in the of archeology, but also in determining the age of sediments, corals, shells, water, soil and others [5]. As research conducted by [6], at the Radiation Chemistry Laboratory of FMIPA Unhas, the LSC method was used in analyzing samples of marine corals originating from the Spermonde Islands in South Sulawesi. Several other studies on determining the age of coral reefs have also been carried out, for example by [7], taking samples around the Spermonde Islands using Karbosorb hydroxide using the LSC method through measurement results, it is known that the age of Spermonde Islands coral reefs is 403.61 years, but the majority of the beaches scattered in the Spermonde Islands do not have the data to see the extent of the coastline of the

Spermonde Islands. Therefore, in this study will be conducted on Panikiang Island, Barru Regency to collect age data on coral reefs in the Spermonde Islands.

## 2. MATERIAL AND METHOD

### 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". Coral samples were taken on the sea around the island in the Spermonde Islands, namely Langkai Island at a depth of 4-5 m at coordinates 4 27'00 " - 5 29'00 " LS and 119 2'00 ' - 119 33'00 'BT

### Physical 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<sub>2</sub>O<sub>2</sub> and 1N NaOH and ultrasonicated for 15 minutes. However, this process often leaves a brownish/orange organic stain on the CaCO<sub>3</sub>. Quick dips (30 seconds to 2 minutes) in a 1:1 mixture of 30% H<sub>2</sub>O<sub>2</sub> and 1N HClO<sub>4</sub> 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<sub>2</sub>O. After drying for several minutes in a 60 °C

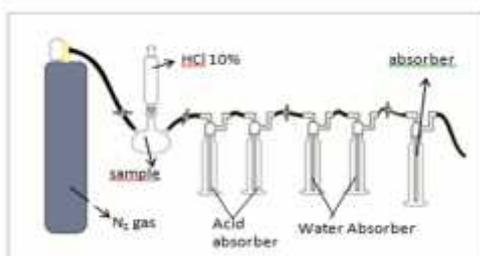
oven, the samples are cooled and reweighed to determine the percent of sample removed. Samples are then crushed in an agate mortar and pestle to facilitate dissolution in the reaction flasks [8].

Samples of coral reefs were washed in running water with brushed several times followed by rinsing with aquades until clean. After physical washing, a coral sample is placed in a container and dried. Chemical washing begins with immersion of coral samples into a mixture of 30% H<sub>2</sub>O<sub>2</sub> and NaOH 1 N 50:50 in a 100 mL beaker and ultrasonic for ± 10 minutes. Then the washing solution is separated from the sample with occasional samples brushed and rinsed again with distilled water (aquades) to remove black stains which are in the narrowest blemish of the sample. Furthermore, the coral reef samples were soaked back in a mixture of 30% H<sub>2</sub>O<sub>2</sub> and 1% 50:50 HClO<sub>4</sub> in a 100 mL beaker for 30 seconds - 2 minutes. The final process in chemical washing is a sample of coral reefs soaked in 10 mL of 10% HCl solution for 15-60 seconds and rinsing again with distilled water (aquades) repeatedly. Furthermore, coral reef samples were dried in an oven at 105°C until dry and weighed again to find out the weight % of the samples lost during the chemical washing process [8].

### Carbon Dioxide Absorption (CO<sub>2</sub>)

Dried coral sample 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 bubbles 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<sub>2</sub> absorbed was quantified from the difference of weight before and after absorption process. The same method is used to absorb CO<sub>2</sub> from Marble for use in the measurement of the Background



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

### Determination of Total Carbon

K<sub>2</sub>CO<sub>3</sub> 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 K<sub>2</sub>CO<sub>3</sub> into a beaker for added BaCl<sub>2</sub> 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.

### Counting Carbon-14

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

### Physical and Chemical Cleaning

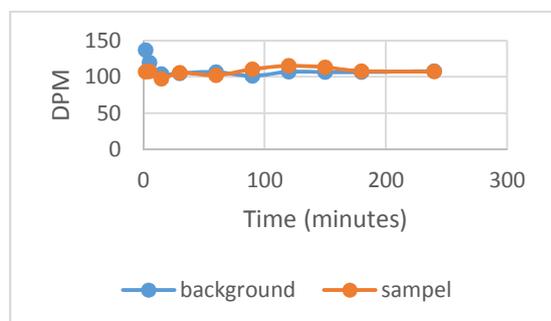
Coral sampel that have been physically and chemically cleaned looked clean and white. The chemical cleaning removed impurities and carbon source on the surface up to 7,94 %. The result of these experiments are not much different from the result of deep-sea coral sample cleanup was done by Adkins et al.<sup>1</sup> and Maming et al.<sup>6</sup> 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 <sup>14</sup>C activity measured on the instrument is expressed in units of Count Per Minute (CPM) which shows the number of β particles produced from <sup>14</sup>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 <sup>14</sup>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<sub>2</sub> absorption using marble as a source of CO<sub>2</sub> 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  $^{14}\text{C}$  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  $^{14}\text{C}$  Sample and Background

Sample	Background
DPM	DPM
108,030	104,690
106,520	104,320
107,210	103,370
106,030	103,320
107,640	102,800
106,430	102,660
106,870	101,920

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  $^{14}\text{C}$  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
107.962	103.297	3,655	0,2496	14,68 ± 4,04	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 carborb was  $342.04 \pm 37,66$  years.

#### 4. CONCLUSIONS

The specific activity of coral sample using ammonium hydroxide as carborb was  $14.68 \pm 4,04$  DPM/g C. The age of coral sample calculated from the specific activity using ammonium hydroxide as carborb was  $342.04 \pm 37,66$  years.

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