



## DETERMINATION OF THE AGE OF SAMALONA ISLAND CORAL REEF THROUGH C-14 ACTIVITY USING LSC METHOD (*LIQUID SCINTILLATION COUNTING*)

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### ABSTRACT

Analysis of <sup>14</sup>C on samples of coral reefs on the Samalona Spermonde Islands vessel through <sup>14</sup>C activity measurements using the LSC (Liquid Scintillation Counting) method was carried out. The preparation sample is carried out physically and chemically. Preparation of coral reefs with chemicals using a mixture of 1N NaOH and 30% H<sub>2</sub>O<sub>2</sub> processed with a mixture of 1% HClO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub> and finally with 10% HCl to produce a clean sample by adding a weight of 5.36%. Carbonate separation was carried out using KOH as a carboxorb to produce K<sub>2</sub>CO<sub>3</sub> solution. The total carbon is determined by the titration method which produces a total carbon of 0.9984 g. Measurement of <sup>14</sup>C activity is done using LSC Hidex 300 SL. Specific activities of coral reef samples obtained were 15.06 ± 3.3613 DPM/gC. Age of coral samples on the island of Samalona in the Spermonde Islands was 130,343 ± 18.4 years.

**Keywords:** Samalona Island, Liquid Scintillation Counting (LSC), Activity <sup>14</sup>C, Coral Reef

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### 1. INTRODUCTION

Samalona is one of the islands in the Spermonde archipelago which is at 119°20'33.4" - 119°20'38.3" BT and 05°07'27.9" - 05°07'33,2" LS with an area of 2.34 ha, District Mariso, Makassar City. Data from the results of the MSDC Unhas study in 2016 showed that the condition of coral reefs on Samalona Island declined, which was around 57% in 2012, to 56% in 2013, then 49% in 2014 and dropped dramatically to 35% in 2015 [1]. One of the factors that influence coral cover is the environmental conditions and

characteristics of the waters. Something similar also happened in the parrots of Samalona. In 2016, the condition of coral reefs on the island of Samalona consisted of three categories, namely bad, medium and good. The condition of coral cover is as good as 65%, while the condition of moderate coral cover is as much as 47% and the condition of bad coral cover is 10% with the dominant coral species is *Acropora sp.*

According to [2], almost all island constituent materials (± 96%) consist of frags of coral reefs of various sizes. The

accumulation of deposited coral reefs if it continues continuously will form a barrier reef. According to Darwin's theory the barrier reef comes from underwater volcanoes, thus the formation of coral reefs is closely related to the expansion of the earth's crust. Determination of the age of dead coral reefs in a waters has enormous benefits in studying the geographic conditions of the origin of the sea coral samples for example to trace and study the formation of a rock formation in a beach. In addition, the determination of the age of coral reefs can also be used to determine the age of real radiocarbon sea water [3].

The study used the LSC method that had been carried out, namely in 2001, Yariato et al. use liquid scintillation counter to determine the optimal conditions in determining the radioactivity of  $^{32}\text{P}$  pest insects. [4], reported the application of DEA as an absentee to determine the age of coral reefs on Barrang Lompo Island by  $\text{CO}_2$  absorption method using liquid scintillation counter. [5], conducted a study to determine the age of sediments in Mamuju Waters through the LSC method. [6], determines the age of selayar aquatic reefs using the  $\text{CO}_2$  absorption method using liquid scintillation counter.

In this study, using the method of LSC (Liquid Scintillation Counting) in determining the age of the coral reefs of the island of Samalona Spermonde Islands based on the measurement of  $^{14}\text{C}$  activity contained in the sample. The selected coral reefs are *Lobophyllia corymboza* because they are quite rare in nature. *L. corymboza* Coral is a member of the *Mussidae* family and is found at a depth of 3-15 meters.

## 2. MATERIAL AND METHOD

### Materials

Times The materials used are: 6 N HCl, 1 M NaOH, 1 M KOH, 30%  $\text{H}_2\text{O}_2$ , 10%  $\text{BaCl}_2$ , Methyl Orange (MO), 1%  $\text{HClO}_4$ , Phenol Thalein (PP), Aqualight LLT, filter paper, distilled water and coral reefs from Samalona Island. Cooking equipment in the form of separating funnels, electric stoves, rulers, mortars, gloves, ovens, hammers and glassware commonly used in laboratories as well as radiation counters from carbon-14 samples, namely LSC Hidex 300 SL.

### Coral Reef Sampling

Sampling was carried out on the island of Samalona. Retrieval at the coordinates of 119°20'27,695 "BT and 05°07'31,974" LS. Sampling of coral reefs from the study location using miser, drill and hammer.

### Washing Physics and Chemistry

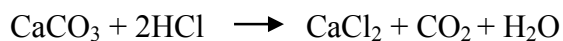
Times The coral reef samples were washed in running water and brushed several times followed by rinsing with distilled water until they were clean. After physical washing, a coral sample is placed in a container and dried. Then coral reefs are cut into several small pieces [7].

Chemical washing begins with immersing coral samples into 30%  $\text{H}_2\text{O}_2$  and 1 N NaOH (1: 1) in a 100 mL beaker and sonicated for  $\pm 10$  minutes. Then the washing solution is separated from the sample with occasional samples brushed and rinsed again with distilled water to remove black stains which are in the narrowest blemish of the sample.

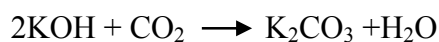
Furthermore, coral reef samples were re-immersed in 30% H<sub>2</sub>O<sub>2</sub> and 1N HClO<sub>4</sub> (1:1) in a 100 mL beaker for 30 seconds to 2 minutes. The final process in chemical washing is a sample of coral reefs soaked in 10 mL of 10% HCl solution for 15-60 seconds and rinsing again with distilled water repeatedly. Furthermore, samples of coral reefs were dried in an oven at a temperature of 105 °C to dryness [7].

### Separation of Carbonate as CO<sub>2</sub>

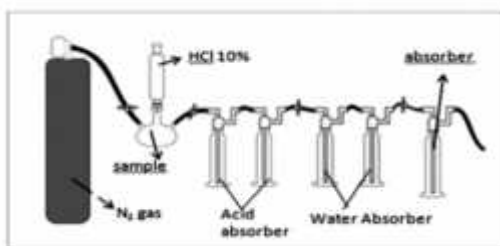
CO<sub>2</sub> analysis in coral reef was carried out as CO<sub>2</sub> gas by KOH. The stages in separating carbonates as CO<sub>2</sub> samples were carried out by adding HCl 10% to 10 grams of sample powder of coral reefs placed in a round bottom flask until HCl 10% was used to react with calcium carbonate in 10 grams of sample. The reactions that occur between calcium carbonate and phosphoric acid are as follows:



CO<sub>2</sub> produced is flowed into the KOH 1 N absorbent solution to produce K<sub>2</sub>CO<sub>3</sub> as in the following reaction:



The scheme of the series of CO<sub>2</sub> absorption samples of coral reefs can be seen in Figure 1.



**Figure 1.** Design of a carbonate separation tool

### Determination of Total Carbon

The total carbon in the sample solution (dissolved K<sub>2</sub>CO<sub>3</sub>) can be calculated from the carbonate concentration obtained from the titration of the sample solution with HCl. The stages in the titration process are as much as 5 mL of sample solution put into erlenmeyer 250 mL then titrated with HCl 5 M, after adding the MO indicator. Then the sample solution was taken back as much as 5 mL into a 250 mL beaker and after that it was added with BaCl<sub>2</sub> 10% until no white carbonate precipitate was formed. Then the solution is filtered and the filtrate obtained is put into 50 mL erlenmeyer and titrated with HCl 5 M, after adding the PP indicator

### Measurement <sup>14</sup>C Activity with LSC Hidex 300 SL

The activity of <sup>14</sup>C in sample is expressed in unit disintegration per minute (DPM) of <sup>14</sup>C. The results of sample enumeration with Liquid Scintillation Counter Hidex 300 SL produced data in CPM units (counts per minute) and TDCR (Triple To Double Coincidence Ratio) or known as efficiency of enumeration (E).

$$E = \frac{\text{Cpm}}{\text{Dpm}} \times 100\%$$

Statistical calculation of radioactive sample using LSC is natural decay calculation on radioactive elements that emit pure beta particles at any time or random decay.

Determination of <sup>14</sup>C activity in coral reef can be determined through enumerating samples with LSC Hidex 300 SL. Mixture sample 8 mL and aqualight

scintillator 12 mL in vial 20 mL. Then, analysis for 5-1440 minutes. The same procedure is done in the background as a comparison.

### Determined Age of Coral Reef

The age of a coral reef sample can be calculated based on a comparison of specific carbon activity ( $15.3 \pm 0.1$  dpm/gr C) to sample specific activities obtained from enumeration using the radiocarbon decay equation:

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

## 3. RESULT AND DISCUSSION

### Physical and Chemical Cleaning Sampling of Coral Reef

Sampling of coral reefs was carried out on Samalona Island, Spermonde Islands. Samalona Island is one of the Spermonde islands which is administratively located in Mariso District, Makassar.



**Figure 2.** Samalona Island Coral Reef

### Cleaning of Coral Reef

In physical washing, samples of coral reef using running water and rinsing with distilled water, washing is able to remove stains or impurities that are easily lost attached to the surface of coral reefs such

as soil and mud. While the chemical washing process that starts from soaking the sample in a mixture of 30%  $H_2O_2$  and 1N NaOH, is able to remove stains that stick to the narrowest gaps in the reef. The second immersion sample in a mixture of 30% acid-base  $H_2O_2$  and 1%  $HClO_4$  was able to remove organic residues mixed with brown / yellow attached to coral polyps which cannot be used in the first soaking. The use of perchloric acid in the second immersion can dissolve 5-6% of the sample weight. Therefore immersion is only carried out about 30 seconds up to 2 minutes.

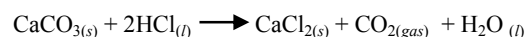
The final process in chemical washing is the sample soaked in 10% HCl for  $\pm$  30 seconds. This immersion is done to reduce the  $CO_2$  adsorbed on the surface of the sample during the washing process.

**Table 1.** Difference weight of samples before and after the cleaning process.

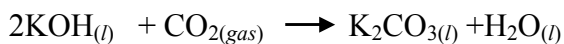
Sample	Before Cleaning (gram)	After Cleaning (gram)	Percentage of Sampel Reduced (%)
Coral Reefs ( <i>L. Corymboza</i> )	201,430	190,640	5,36 %

### Separation of Carbonate in Samples

Coral reefs contain calcium carbonate. The carbonate separation process of coral samples was carried out by adding HCl 10% to coral samples which placed into a round bottom flask. Reaction occurs between calcium carbonate and phosphoric acid:



$CO_2$  gas absorbed by the KOH solution through chemical reaction will produce dissolved  $K_2CO_3$  with the following reaction:



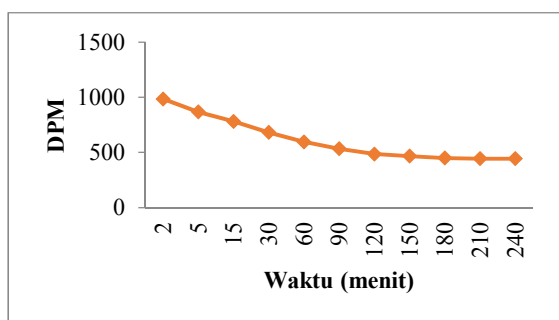
### Determination of Carbon Total in Samples

Determination of total carbon was carried out using the titration method using 5M HCl. Calculation of total carbon is carried out in order to determine the weight of the gram of carbon contained in the sample that will be used in calculating the specific activity of carbon-14 contained in coral reef samples. This specific activity is the basis for calculating the age of the sample. The results of calculating total carbon in coral reef samples is 0.9984 g.

### Measurement Activity $^{14}\text{C}$ Sample with LSC Hidex 300 SL

The process of measuring  $^{14}\text{C}$  activity in a coral sample was carried out by enumerating a mixture of 8 mL sample solution and 12 mL scintillator in a 20 mL vial. Sample enumeration was carried out in 2 stages, namely, the stage of determining the optimum enumeration time and the stage of determining the average enumeration value at the optimum time.

Graph of the DPM value of the sample for the time of counting as shown in Figure 3.



**Figure 3.** Graph of the DPM value of the sample for the time of counting

Based on Figure 3, there is a periodic decrease in DPM over time. However, at 180-240 minutes the DPM decrease was not significant. The most insignificant or stationary decrease occurred at 210 minutes with enumeration efficiency (TDCR) of 0.593, so that the optimum enumeration time was 210 minutes. The sample is then chopped repeatedly during the optimum time. The results of the count at the optimum time were used to calculate the specific activity of  $^{14}\text{C}$  in the sample. The results of enumeration samples at the optimum enumeration time 210 minutes with 10 repetitions can be seen in Table 2.

**Table 2.** Data on enumeration results at the optimum time sample of the coral reefs of the island of Samalona, spermonde islands with LSC Hidex 300 SL devices with 10 repetitions

No	Chopping Time (Minutes)	Decay Activity (DPM)
1	210	443,540
2	210	446,790
3	210	448,260
4	210	448,500
5	210	443,370
6	210	446,010
7	210	437,980
8	210	445,400
9	210	441,440
10	210	442,690
Average		444,398

### Determination of Coral Specific Sample Activities

The average specific activity (AS) of the sample from the calculation of DPM per unit of carbon mass was obtained at

$15.06 \pm 3.36$  DPM / gC. Calculation of coral reef specific sample activities can be seen in Annex 7. The average value of specific activity of  $^{14}\text{C}$  obtained from the sample is smaller than the average specific activity value of modern carbon standards, which is  $15.3 \pm 0.1$  DPM / gC. The activity obtained in the sample shows that carbon atom decay takes place every minute (DPM) in one gram of carbon.

### Calculation Age of Coral Reefs

The age of coral reef is determined by comparison with  $^{14}\text{C}$  radioactivity from living sample or standard ( $A_0$ ) and Radioactivity  $^{14}\text{C}$  in the sample ( $A_t$ ).

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

Where :

$A_t$  = Radioactivity of the  $^{14}\text{C}$  isotope in the sample

$A_0$  =  $^{14}\text{C}$  isotope radioactivity when the plant or animal lives ( $15.3 \pm 0.1$ ) DPM (Libby, 1960)

$t_{1/2}$  = half-life =  $5730 \pm 50$  years

$\ln 2 = 0.693$

Based on the calculations performed, the age of the coral reef was around  $130,343 \pm 18.4$  years. The standard deviation value obtained is quite large, this occurs because of several factors including the process of repeating a small number and this method is difficult to determine in absolute terms the measurement of age of the sample in the range of tens of thousands of years.

### 4. CONCLUSIONS

Based on the results of research on samples of the coral reefs of the island of Samalona Spermonde Islands with the method of LSC (Liquid Scintillation Counting), conclusions can be drawn:

1. The value of the specific activity of  $^{14}\text{C}$  on the determination of the age of Samalona Island's Spermonde Island coral reef based on  $^{14}\text{C}$  activity measurements is  $15.06 \pm 3.3613$  DPM/gC.
2. The age of Samalona Island's Spermonde Island coral reef sample based on  $^{14}\text{C}$  activity measurements was  $130,343 \pm 18.4$  years.

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